Loss Prevention in the Process Industries

Volume 2

This book is dedicated to

Herbert Douglas Lees (1860–1944), gas engineer;
Frank Priestman Lees (1890–1916), gas engineer;
Herbert Douglas Lees (1897–1955), gas engineer;
David John Lees (1936–), agricultural engineer;
Frank Lyman MacCallum (1893–1955), mining engineer and missionary;
Vivien Clare Lees (1960–), plastic and hand surgeon
Harry Douglas Lees (1962–), restaurateur
and their families

'They do not preach that their God will rouse them a little before
the nuts work loose.
They do not teach that His Pity allows them to drop their job when
they dam'-well choose.
As in the thronged and the lighted ways, so in the dark and the
desert they stand,
Wary and watchful all their days that their brethren's days may be
long in the land.'

Rudyard Kipling (The Sons of Martha, 1907)

Wo einer kommt and saget an,
Er hat es allen recht getan,
So bitten wir diesen lieben Herrn,
Er wöll uns solche Kunste auch lehrn

(Whoever is able to say to us
'I have done everything right',
We beg that honest gentleman
To show us how it is done)

Inscription over the 'Zwischenbau' adjoining the Rathaus in Brandenburg-on-the-Haven
(quoted by Prince B.H.M. von Bulow in *Memoirs*, 1932)

If the honeye that the bees gather out of so manye floure of herbes... that are growing in other mennis medowes... may justly be called the bees' honeye... so maye I call it that I have... gathered of manye good autores... my booke.
William Turner (quoted by A. Scott-James in *The Language of the Garden: A Personal Anthology*)

By the same author:

A.W. Cox, F.P. Lees and M.L. Ang (1990): *Classification of Hazardous Locations* (Rugby: Institution of Chemical Engineers)

Elwyn Edwards and Frank P. Lees (1973): *Man and Computer in Process Control* (London: Institution of Chemical Engineers)

Elwyn Edwards and Frank P. Lees (eds) (1974): *The Human Operator in Process Control* (London: Taylor & Francis)

Frank P. Lees and M.L. Ang (1989): *Safety Cases* (London: Butterworths)

Loss Prevention in the Process Industries

Hazard Identification, Assessment and Control

Volume 2

Second edition

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Preface to Second Edition

The first edition of this book appeared in 1980, at the end of a decade of rapid growth and development in loss prevention. After another decade and a half the subject is more mature, although development continues apace. In preparing this second edition it has been even more difficult than before to decide what to put in and what to leave out.

The importance of loss prevention has been underlined by a number of disasters. Those at San Carlos, Mexico City, Bhopal and Pasadena are perhaps the best known, but there have been several others with death tolls exceeding 100. There have also been major incidents in related areas, such as those on the Piper Alpha oil platform and at the nuclear power stations at Three Mile Island and Chernobyl.

Apart from the human tragedy, it has become clear that a major accident can seriously damage even a large international company and may even threaten its existence, rendering it liable to severe damages and vulnerable to takeover.

Accidents in the process industries have given impetus to the creation of regulatory controls. In the UK the Advisory Committee on Major Hazards made its third and final report in 1983. At the same time the European Community was developing its own controls which appeared as the EC Directive on Major Accident Hazards. The resulting UK legislation is the NIHHS Regulations 1982 and the CIMAH Regulations 1984. Other members of the EC have brought in their own legislation to implement the Directive. There have been corresponding developments in planning controls...

An important tool for decision-making on hazards is hazard assessment. The application of quantitative methods has played a crucial role in the development of loss prevention, but there has been lively debate on the proper application of such assessment, and particularly on the estimation and evaluation of the risk to the public.

Hazard assessment involves the assessment both of the frequency and of the consequences of hazardous events. In frequency estimation progress has been made in the collection of data and creation of data banks and in fault tree synthesis and analysis, including computer aids. In consequence assessment there has been a high level of activity in developing physical models for emission, vaporization and gas dispersion, particularly dense gas dispersion; for pool fires, fireballs, jet flames and engulfing fires; for vapour cloud explosions; and for boiling liquid expanding vapour explosions (BLEVEs). Work has also been done on injury models for thermal radiation, explosion overpressure and toxic concentration, on models of the density and other characteristics of the exposed population, and on shelter and escape.

Some of these topics require experimental work on a large scale and involving international cooperation. Large scale tests have been carried out at several sites on dense gas dispersion and on vapour cloud fires and explosions. Another major cooperative research programme has been that of DIERS on venting of chemical reactors.

The basic approach developed for fixed installations on shore has also been increasingly applied in other fields. For transport in the UK the *Transport Hazards Report* of the Advisory Committee on Dangerous Substances represents an important landmark. Another application is in the offshore oil and gas industry, for which the report on the Piper Alpha disaster, the *Cullen Report*, constitutes a watershed.

As elsewhere in engineering, computers are in widespread use in the design of process plants, where computer aided design (CAD) covers physical properties, flowsheeting, piping and instrument diagrams, unit operations and plant layout. There is increasing use of computers for failure data retrieval and analysis, reliability and availability studies, fault tree synthesis and analysis and consequence modelling, while more elusive safety expertise is being captured by computer-based expert systems.

The subject of this book is the process industries, but the process aspects of related industries, notably nuclear power and oil and gas platforms are briefly touched on. The process industries themselves are continually changing. In the last decade one of the main changes has been increased emphasis on products such as pharmaceuticals and agrochemicals made by batch processes, which have their own particular hazards.

All this knowledge is of little use unless it reaches the right people. The institutions which educate the engineers who will be responsible for the design and operation of plants handling hazardous materials have a duty to make their students aware of the hazards and at least to make a start in gaining competence in handling them.

I would like again to thank for their encouragement the heads of the Department of Chemical Engineering at Loughborough, Professors D.C. Freshwater, B.W. Brooks and M. Streat; our Industrial Professors T.A. Kletz and H.A. Duxbury and Visiting Professor S.M. Richardson; my colleagues, past and present, in the Plant Engineering Group, Mr R.J. Aird, Dr P.K. Andow, Dr M.L. Ang, Dr P.W.H. Chung, Dr D.W. Edwards, Dr P. Rice and Dr A.G. Rushton – I owe a particular debt to the latter; the members of the ACMH, chaired by Professor B.H. Harvey; the sometime directors of Technica Ltd, Dr D.H. Slater, Mr P. Charsley, Dr P.J. Comer, Dr R.A. Cox, Mr T. Gjerstad, Dr M.A.F. Pyman, Mr C.G. Ramsay, Mr M.A. Seaman and Dr R. Whitehouse; the members of the IChemE Loss Prevention Panel; the IChemE's former Loss Prevention Officer, Mr B.M. Hancock; the members of the IChemE Loss Prevention Study Group and of the Register of Safety Professionals; the editorial staff of the IChemE, in particular Mr B. Brammer; numerous members of the Health and Safety Executive, especially Dr A.C. Barrell, Mr J. Barton, Dr D.A. Carter, Mr K. Cassidy, Mr P.J.

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FRANK P. LEES
Loughborough,
1994

Preface to First Edition

Within the past ten or fifteen years the chemical and petroleum industries have undergone considerable changes. Process conditions such as pressure and temperature have become more severe. The concentration of stored energy has increased. Plants have grown in size and are often single-stream. Storage has been reduced and interlinking with other plants has increased. The response of the process is often faster. The plant contains very large items of equipment. The scale of possible fire, explosion or toxic release has grown and so has the area which might be affected by such events, especially outside the works boundary.

These factors have greatly increased the potential for loss both in human and in economic terms. This is clear both from the increasing concern of the industry and its insurers and from the historical loss statistics.

The industry has always paid much attention to safety and has a relatively good record. But with the growing scale and complexity involved in modern plants the danger of serious large-scale incidents has been a source of increasing concern and the adequacy of existing procedures has been subjected to an increasingly critical examination.

Developments in other related areas have also had an influence. During the period considered there has been growing public concern about the various forms of pollution, including gaseous and liquid effluents and solid wastes and noise.

It is against this background that the loss prevention approach has developed. It is characteristic of this approach that it is primarily concerned with the problems caused by the depth of technology involved in modern processes and that it adopts essentially an engineering approach to them. As far as possible both the hazards and the protection are evaluated quantitatively.

The clear recognition by senior management of the importance of the loss prevention problem has been crucial to these developments. Progress has been made because management has been prepared to assign to this work many senior and capable personnel and to allocate the other resources necessary.

The management system is fundamental to loss prevention. This involves a clear management structure with well defined line and advisory responsibilities staffed by competent people. It requires the use of appropriate procedures, codes of practice and standards in the design and operation of plant. It provides for the identification, evaluation and reduction of hazards through all stages of a project from research to operation. It includes planning for emergencies.

The development of loss prevention can be clearly traced through the literature. In 1960 the Institution of Chemical Engineers held the first of a periodic series of symposia on *Chemical Process Hazards with Special Reference to Plant Design*. The Dow Chemical Company published its *Process Safety Manual* in 1964. The American Institute of Chemical Engineers started in 1967 an annual series of symposia on Loss Prevention. The European Federation of Chemical Engineers' symposium on *Major Loss Prevention in the Process Industries* at Newcastle in 1971 and the Federation's symposium on *Loss Prevention and Safety Promotion in the Process Industries* (Buschmann, 1974) at Delft are further milestones.

Another indicator is the creation in 1973 by the Institution of Chemical Engineers Engineering Practice Committee of a Loss Prevention Panel under the chairmanship of Mr T.A. Kantyka.

In the United Kingdom the Health and Safety at Work etc. Act 1974 has given further impetus to loss prevention. The philosophy of the *Robens Report* (1972), which is embodied in the Act, is that of self-regulation by industry. It is the responsibility of industry to take all reasonable measures to assure safety. This philosophy is particularly appropriate to complex technological systems and the Act provides a flexible framework for the development of the loss prevention approach.

The disaster at Flixborough in 1974 has proved a turning point. This event has led to a much more widespread and intense concern with the loss prevention problem. It has also caused the government to set up in 1975 an Advisory Committee on Major Hazards. This committee has made far-reaching recommendations for the identification and control of major hazard installations.

It will be apparent that loss prevention differs somewhat from safety as traditionally conceived in the process industries. The essential difference is the much greater engineering content in loss prevention.

This is illustrated by the relative effectiveness of inspection in different processes. In fairly simple plants much can be done to improve safety by visual inspection. This approach is not adequate, however, for the more technological aspects of complex processes.

For the reasons given above loss prevention is currently a somewhat fashionable subject. It is as well to emphasize, therefore, that much of it is not new, but has been developed over many years by engineers whose patient work in an often apparently unrewarding but vital field is the mark of true professionalism.

It is appropriate to emphasize, moreover, that accidents arising from relatively mundane situations and activities are still responsible for many more deaths and injuries than those due to advanced technology.

Nevertheless, loss prevention has developed in response to the growth of a new problem, the hazard of high technology processes, and it does have a distinctive approach and some novel techniques. Particularly characteristic are the emphasis on matching the management system to the depth of technology in the installation, the techniques developed for identifying hazards, the principle and methods of quantifying hazards, the application of reliability assessment, the

practice of planning for emergencies and the critique of traditional practices or existing codes, standards or regulations where these are outdated by technological change.

There is an enormous, indeed intimidating, literature on safety and loss prevention. In addition to the symposia already referred to, mention may be made of the *Handbook of Safety and Accident Prevention in Chemical Operations* by Fawcett and Wood (1965); the *Handbook of Industrial Loss Prevention* by the Factory Mutual Engineering Corporation (1967); and the *Industrial Safety Handbook* by Handley (1969, 1977). These publications, which are by multiple authors, are invaluable source material.

There is a need, however, in the author's view for a balanced and integrated textbook on loss prevention in the process industries which presents the basic elements of the subject, which covers the recent period of intense development and which gives a reasonably comprehensive bibliography. The present book is an attempt to meet this need.

The book is based on lectures given to undergraduate and postgraduate students at Loughborough over a period of years and the author gladly acknowledges their contribution.

Loss prevention is a wide and rapidly developing field and is therefore not an easy subject for a book. Nevertheless, it is precisely for these reasons that the engineer needs the assistance of a textbook and that the attempt has been considered justified.

The structure of the book is as follows. Chapter 1 deals with the background to the historical development of loss prevention, the problem of large, single-stream plants, and the differences between loss prevention and conventional safety, and between loss prevention and total loss control; Chapter 2 with hazard, accident and loss, including historical statistics; Chapter 3 with the legislation and legal background; Chapter 4 with the control of major hazards; Chapter 5 with economic and insurance aspects; Chapter 6 with management systems, including management structure, competent persons, systems and procedures, standards and codes of practice, documentation and auditing arrangements; Chapter 7 with reliability engineering, including its application in the process industries; Chapter 8 with the spectrum of techniques for identifying hazards from research through to operation; Chapter 9 with the assessment of hazards, including the question of acceptable risk; Chapter 10 with the siting and layout of plant; Chapter 11 with process design, including application of principles such as limitation of inventory, consideration of known hazards associated with chemical reactors, unit processes, unit operations and equipments, operating conditions, utilities, particular chemicals and particular processes and plants, and checking of operational deviations; Chapter 12 with pressure system design, including properties of materials, design of pressure vessels and pipework, pressure vessel standards and codes, equipment such as heat exchangers, fired heaters and rotating machinery, pressure relief and blowdown arrangements, and failure in pressure systems; Chapter 13 with design of instrumentation and control systems, including regular instrumentation, process computers and protective systems; Chapter 14 with human factors in process control, process operators, computer aids and human error; Chapter 15 with loss of containment and dispersion of material; Chapter 16 with fire, flammability characteristics, ignition sources, flames and particular types of process fire, effects of fire and fire prevention, protection and control; Chapter 17 with explosion, explosives, explosion energy, particular types of process explosion such as confined explosions, unconfined vapour cloud explosions and dust explosions, effects of explosion and explosion prevention, protection and relief; Chapter 18 with toxicity of chemicals, toxic release and effects of toxic release; Chapter 19 with commissioning and inspection of plant; Chapter 20 with plant operation; Chapter 21 with plant maintenance and modification; Chapter 22 with storage; Chapter 23 with transport, particularly by road, rail and pipeline; Chapter 24 with emergency planning both for works and transport emergencies; Chapter 25 with various aspects of personal safety such as occupational health and industrial hygiene, dust and radiation hazards, machinery and electrical hazards, protective clothing and equipment, and rescue and first aid; Chapter 26 with accident research; Chapter 27 with feedback of information and learning from accidents; Chapter 28 with safety systems, including the roles of safety managers and safety committees and representatives. There are appendices on Flixborough, Seveso, case histories, standards and codes, institutional publications, information sources, laboratories and pilot plants, pollution and noise, failure and event data, Canvey, model licence conditions for certain hazardous plants, and units and unit coversions.

Many of the matters dealt with, such as pressure vessels or process control, are major subject areas in their own right. It is stressed, therefore, that the treatment given is strictly limited to loss prevention aspects. The emphasis is on deviations and faults which may give rise to loss.

In engineering in general and in loss prevention in particular there is a conflict between the demand for a statement of basic principles and that for detailed instructions. In general, the first of these approaches has been adopted, but the latter is extremely important in safety, and a considerable amount of detailed material is given and references are provided to further material.

The book is intended as a contribution to the academic education of professional chemical and other engineers. Both educational and professional institutions have long recognized the importance of education in safety. But until recently the rather qualitative, and indeed often exhortatory, nature of the subject frequently seemed to present difficulties in teaching at degree level. The recent quantitative development of the subject goes far towards removing these objections and to integrating it more closely with other topics such as engineering design.

In other words, loss prevention is capable of development as a subject presenting intellectual challenge. This is all to the good, but a note of caution is appropriate. It remains true that safety and loss prevention depend primarily on the hard and usually unglamorous work of engineers with a strong sense of responsibility, and it is important that this central fact should not be obscured.

For this reason the book does not attempt to select particular topics merely because a quantitative treatment is possible or to give such a treatment as an academic

exercise. The subject is too important for such an approach. Rather the aim has been to give a balanced treatment of the different aspects and a lead in to further reading.

It is also hoped that the book will be useful to practising engineers in providing an orientation and entry to unfamiliar areas. It is emphasized, however, that in this subject above all others, the specialized texts should be consulted for detailed design work.

Certain topics which are often associated with loss prevention, for example included in loss prevention symposia, have not been treated in detail. These include, for example, pollution and noise. The book does not attempt to deal in detail with total loss control, but a brief account of this is given.

The treatment of loss prevention given is based mainly on the chemical, petrochemical and petroleum industries, but much of it is relevant to other process industries, such as electrical power generation (conventional and nuclear), iron and steel, gas, cement, glass, paper and food.

The book is written from the viewpoint of the United Kingdom and, where differences exist within the UK, of England. This point is relevant mainly to legislation.

Reference is made to a large number of procedures and techniques. These do not all have the same status. Some are well established and perhaps incorporated in standards or codes of practice. Others are more tentative. As far as possible the attempt has been made to give some indication of the extent to which particular items are generally accepted.

There are probably also some instances where there is a degree of contradiction between two approaches given. In particular, this may occur where one is based on engineering principles and the other on relatively arbitrary rules-of-thumb.

The book does not attempt to follow standards and codes of practice in drawing a distinction between the words *should*, *shall* and *must* in recommending particular practices and generally uses only the former. The distinction is important, however, in standards and codes of practice and it is described in Appendix 4[a].

An explanation of some of the terms used is in order at this point. Unfortunately there is at present no accepted terminology in this field. In general, the problems considered are those of loss, either of life or property. The term *hazard* is used to describe the object or situation which constitutes the threat of such loss. The consequences which might occur if the threat is realized are the *hazard potential*. Associated with the hazard there is a risk, which is the probability of the loss occurring. Such a risk is expressed as a *probability* or as a *frequency*. Probability is expressed as a number in the range 0 to 1 and is dimensionless; frequency is expressed in terms of events per unit time, or sometimes in other units such as events per cycle or per occasion. Rate is also used as an alternative to frequency and has the same units.

The analysis of hazards involves qualitative *hazard identification* and quantitative *hazard assessment*. The latter term is used to describe both the assessment of hazard potential and of risk. The assessment of risk only is described as *risk assessment*.

In accident statistics the term *Fatal Accident Frequency Rate* (FAFR) has some currency. The last two terms are tautologous and the quantity is here referred to as *Fatal Accident Rate* (FAR).

Further treatments of terminology in this field are given by BS 4200: 1967, by Green and Bourne (1962), by the Council for Science and Society (1977) and by Harvey (1979b).

Notation is defined for the particular chapter at the point where the symbols first occur. In general, a consistent notation is used, but well established equations from standards, codes and elsewhere are usually given in the original notation. A consolidated list of the notation is given at the end of chapters in which a large number of symbols is used.

The units used are in principle SI, but the exceptions are fairly numerous. These exceptions are dimensional equations, equations in standards and codes, and other equations and data given by other workers where conversion has seemed undesirable for some reason. In cases of conversion from a round number it is often not clear what degree of rounding off is appropriate. In cases of description of particular situations it appears pedantic to make the conversion where a writer has referred, for example, to a 1 inch pipe.

Notes on some of the units used are given in Appendix 12[a]. For convenience a unit conversion table is included in this appendix. Numerical values given by other authors are generally quoted without change and numerical values arising from conversion of the units of data given by other authors are sometimes quoted with an additional significant figure in order to avoid excessive rounding of values.

Some cost data are quoted in the book. These are given in pounds or US dollars for the year quoted.

A particular feature of the book is a fairly extensive bibliography of some 5000 references. These references are consolidated at the end of the book rather than at the end of chapters, because many items are referred to in a number of chapters. Lists of selected references on particular topics are given in table form in the relevant chapters.

Certain institutions, however, have a rather large number of publications which it is more convenient to treat in a different manner. These are tabulated in Appendices 4[a] and 5[a], which contain some 2000 references. There is a cross-reference to the institution in the main reference list.

In many cases institutions and other organizations are referred to by their initials. In all cases the first reference in the book gives the full title of the organization. The initials may also be looked up in the Author Index, which gives the full title.

A reference is normally given by quoting the author and, in brackets, the date, e.g. Kletz (1971). Publications by the same author in the same year are denoted by letters of the alphabet a, b, c, etc., e.g. Allen (1977a), while publications by authors of the same surname and in the same year are indicated for convenience by an asterisk against the year in the list of references. In addition, the author's initials are given in the main text in cases where there may still be ambiguity. Where a date has not been determined this is indicated as n.d.

[a]Appendices 4, 5 and 12 in the first edition correspond to Appendices 27, 28 and 30, respectively, in this second edition.

In the case of institutional publications listed in Appendices 4[a] and 5[a] the reference is given by quoting the insitution and, in brackets, the date, the publication series, e.g. HSE (1965 HSW Bklt 34) or the item number, e.g. IChemE (1971 Item 7). For institutional publications with a named author the reference is generally given by quoting the author and, in brackets, the initials of the institution, the date and the publication series or item number, e.g. Eames (UKAEA 1965 Item 4).

The field of loss prevention is currently subject to very rapid change. In particular, there is a continuous evolution of standards and codes of practice and legislation. It is important, therefore, that the reader should make any necessary checks on changes which may have occurred.

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Professor H.A. Duxbury and Dr A.J. Wilday have been good enough comment on Chapter 17, Sections 17.16–17.21. Professor Duxbury has also contributed Appendix 13 on safety factors in simple relief systems.

The responsibility for the text is mine alone.

Terminology

Attention is drawn to the availability in the literature of a number of glossaries and other aids to terminology. Some British Standard glossaries are given in Appendix 27 and other glossaries are listed in Table 1.1.

Notation

In each chapter a given symbol is defined at the point where it is first introduced. The definition may be repeated if there has been a significant gap since it was last used. The definitions are summarized in the notation given at the end of the chapter. The notation is global to the chapter unless redefined for a section. Similarly, it is global to a section unless redefined for a subsection and global to a subsection unless redefined for a set of equations or a single equation. Where appropriate, the units are given, otherwise a consistent system of units should be used, SI being the preferred system. Generally the units of constants are not given; where this is the case it should not be assumed that a constant is dimensionless.

Use of References

The main list of references is given in the section entitled References, towards the end of the book. There are three other locations where references are to be found. These are Appendix 27 on standards and codes; Appendix 28 on institutional publications; and in the section entitled Loss Prevention Bulletin which follows the References.

The basic method of referencing an author is by surname and date, e.g. Beranek (1960). Where there would otherwise be ambiguity, or where there are numerous references to the same surname, e.g. Jones, the first author's initials are included, e.g. A. Jones (1984). Further guidance on names is given at the head of the section References.

References in Appendices 27 and 28 are by institution or author. Some items in these appendices have a code number assigned by the institution itself, e.g. API (1990 Publ. 421), but where such a code number is lacking, use is generally made of an item number separated from the date by a slash, e.g. IChemE (1971/13). Thus typical entries are

API Std 2000: 1992	a standard, found in Appendix 27 under American Petroleum Institute
API (1990 Publ. 421)	an institutional publication, found in Appendix 28 under American Petroleum Institute
HSE (1990 HS(G) 51)	an institutional publication, found in Appendix 28 under Health and Safety Executive, Guidance Booklets, HS(G) series
Coward and Jones (1952 BM Bull. 503)	an institutional publication, found in Appendix 28 under Bureau of Mines, Bulletins

Institutional acronyms are given in the section Acronyms which precedes the Author Index.

There are several points of detail which require mention concerning Appendix 28. (1) The first part of the appendix contains publications of a number of institutions and the second part those of the Nuclear Regulatory Commission. (2) The Fire Protection Association publications include a number of series which are collected in the *Compendium of Fire Safety Data* (CFSD). A typical reference to this is FPA (1989 CFSD FS 6011). (3) The entries for the Health and Safety Executive are quite extensive and care may be needed in locating the relevant series. (4) The publications of the Safety and Reliability Directorate appear under the UK Atomic Energy Authority, Safety and Reliability Directorate. A typical reference is Ramskill and Hunt (1987 SRD R354). These publications are immediately preceded by the publications of other bodies related to the UKAEA, such as the Health and Safety Branch, the Systems Reliability Service and the National Centre for Systems Reliability.

References to authors in the IChemE *Loss Prevention Bulletin* are in the style Eddershaw (1989 LPB 88), which refers to issue 88 of the bulletin.

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The first of the major hazards in process plant is fire. Fire in the process industries causes more serious accidents than explosion or toxic release, although the accidents in which the greatest loss of life and damage occur are generally caused by explosion. Fire is normally regarded as having a disaster potential less than explosion or toxic release. One of the worst explosion hazards, however, is usually considered to be that of an explosion of a vapour cloud which has drifted over a populated area, and in this case the difference in the number of casualties caused by a flash fire rather than an xplosion in the cloud may be relatively small.

Fire is therefore a serious hazard. The Second *Report* of the Advisory Committee on Major Hazards (ACMH) (Harvey, 1979b) refers in particular to vapour cloud fires and to the description of fires given by V.C. Marshall (1977a):

> It can be said that such clouds will start to burn around their outer envelopes and will 'lift off' to form fireballs. Such fires are dangerous in the extreme. When formed of hydrocarbons, they are luminous and radiate heat which can cause fatal burns to bystanders, and which can ignite wood and paper; for example, they have been known to set fire to the interior of office blocks. As fireballs rise they produce mushroom clouds, in the stalks of which are formed violent upward convection currents which can suck up and ignite debris, and scatter burning brands over a wide area. Such an occurrence can clearly cause damage far beyond the normal safety distance of what are termed conventional fires.

Vapour cloud, or flash fires and fireballs radiate intense heat which can be lethal. Another lethal effect is the depletion of oxygen in the atmosphere caused by a flash fire. Although the Flixborough disaster was primarily a vapour cloud explosion, the latter was also accompanied by a large flash fire in part of the cloud and this fire was responsible for some of the deaths which occurred. Flash fires can also do considerable damage to plant. In buildings fire is the main threat, and can cause great damage and loss of life.

There are in the UK a number of bodies concerned with fire and fire protection. These include the fire services and organizations such as the British Fire Services Association, the professional institutions such as the Institution of Fire Engineers (IFE), the insurance organizations such as the Fire Offices Committee, the research establishments such as the Fire Research Station (FRS) and the educational institutions such as the Fire Protection Association (FPA) and the Department of Fire Engineering at Edinburgh University.

In the USA the relevant bodies include: in insurance, the National Board of Fire Underwriters, the Industrial Risk Insurers (IRI) (formerly the Factory Mutual Engineering Corporation (FMEC)); in research, the Underwriters Laboratories (UL), the Bureau of Mines (BM) and the Combustion Institute; and in the formulation of codes and research, the National Fire Protection Association (NFPA).

There is a voluminous literature on fire and fire protection. Only a few selected items particularly relevant to process plant can be instanced here. These are *Safety in Petroleum Refining and Related Industries* (Armistead, 1959), *Chemical Fires and Chemicals at Fires* (IFE, 1962), *Fire Protection Handbook* (Vervalin, 1964a, 1973a), *Handbook of Industrial Loss Prevention* (FMEC, 1967), *A Guide to Fire Prevention in the Chemical Industry* (BCISC, 1968/7), *Storage and Handling of Petroleum Liquids: Practice and Law* (J.R. Hughes, 1970), *Background Notes on Fire and its Control* (FPA, 1971/14), *Heat Transfer in Fires* (Blackshear, 1974), *Manual of Firemanship* (Home Office, 1974–), *An Introduction to Fire Dynamics* (Drysdale, 1985) and *Fire Protection Handbook* (NFPA, 1991/8).

Information on numerous aspects of fire and fire protection is given in the FPA *Compendium of Fire Safety Data Sheets* (1974–), which covers the following topics. Volume 1: (1) organization of fire safety and (2) management of fire risks. Volume 2: (3) industrial and process fire safety and (4) occupancy fire safety. Volume 3: (5) housekeeping and general fire precautions and (6) nature and behaviour of fire. Volume 4: (7) information sheets on hazardous materials. Volume 5: (8) fire protection equipment and systems, (9) security precautions and (10) arson. Volume 6: (11) design guides and (12) building products.

A relevant standard is BS 5908: 1990 *Code of Practice for Fire Precautions in Chemical Plant*. This contains the following sections:

(1) general;
(2) legal requirements;
(3) principles of initiation, spread and extinction of fire;
(4) site selection and layout;
(5) buildings and structures;
(6) storage and movement of materials;
(7) design of process plant;
(8) operation of process plant;
(9) maintenance of process plant;
(10) fire prevention;
(11) fire defence;
(12) works fire brigades;
(13) classification of fires and selection of extinguishing media;
(14) fixed fire fighting systems;
(15) portable and transportable appliances;
(16) organization of emergency procedures.

Most of these aspects are considered in the present chapter, but some are dealt with elsewhere, notably legal aspects, plant siting and layout, storage, maintenance and emergency procedures, which are treated in Chapters 3, 10, 22, 21 and 24, respectively.

US codes include the National Fire Codes of the NFPA. A selection of the codes relevant to process plant is given in Appendix 27.

Selected references on fire and on fire, prevention, protection and control are given in Tables 16.1 and 16.2, respectively. In addition, many of the publications listed in Appendices 27 and 28 are concerned with fire.

Table 16.1 *Selected references on fire*

FRS (Appendix 28); NRC (Appendix 28 *Fire*, *Fire Protection*); von Schwartz (1904–); McCarthy (1943); Smart (1947); Cameron (1948); Spiers (1950); Prentiss (1951); Bowden (1953); Spalding (1955); Wise and Agoston (1958); Simms, Hird and Wraigh (1960); B. Lewis and von Elbe (1961, 1987); FPA (1965 CFSD NB4, 1965/4, 1971/14, 1988 CFSD NB2, 1989 CFSD NB1);

Risinger (1964a–f,h,j); Vervalin (1964a, 1966, 1972a, 1973a,g, 1975a,f); F.A. Williams (1965); Zabetakis (1965); Waugh (1966); FMEC (1967); W.B. Howard (1970b); Custer (1972); de Ris, Kanury and Yuen (1973); Sylvia (1973); Home Office (1974– *Manual of Firemanship*); Ottoson (1974); Raj and Kalelkar (1974); Skramstad (1974); Wharry and Hirst (1974); Eisenberg, Lynch and Breeding (1975); AIChE (1976/69); Drysdale (1976b, 1985); Kletz (1976h, 1979a); Rasbash (1977a, 1979/80); Stull (1977); R. King and Magid (1979); Lock (1979); Solomon (1980); P.H. Thomas (1980); J.G. Marshall and Rutledge (1982); Pantony and Smith (1982); Tsuchiya (1982); ASME (1983/52); Hofman (1983); Hottel (1984); BRE (1985 BR 60); Schultz (1985); Babrauskas (1986a); Kuo (1986); de Ris (1986); Harmathy and Mehaffey (1987); Emms (1988); Bagster and Pitblado (1989); ILO (1989); J.B. Moss (1989); Mudan (1989b); C.D. Woodward (1989); V.C. Marshall (1990b); Pineau *et al.* (1991); CPD (1992a,b); Carhart (1994)
BS 5908: 1980

Fire statistics, fire costs (*see also* Table 2.1)
BIA (annual report, 1975); Anon. (1960–61); Chandler (1969); BRE (1970– UK Fire and Loss Statistics); CIA (1970/3); FRS (1972 Fire Res. Notes 910, 920, 1973 Fire Res. Notes 978, 981, 1974 Fire Res. Note 1011); H.D. Taylor and Redpath (1971); Vervalin (1972c, 1973d, 1974a, 1975c, 1976b, 1977, 1978a,b); Anon. (1974e,g,m); Tovey (1974); Duff (1975); Fry (1975); Redpath (1976); Rutstein (1979b); Rutstein and Clarke (1979); Beard (1981/82); Ramachandran (1982, 1988); Anon. (1983h)

Fire rating
UL (n.d./b); Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); Law (1991)

Fire properties of materials, fire tests (*see also* Tables 8.1, 11.1, 11.18, 16.3, 17.2 and *17.62*)
BRE (n.d./4–6, 1974 CP 91/74, 1975 CP 36/75); SMRE (Fire 1, 3, 6); Burgoyne and Richardson (1948); Burgess and Zabetakis (1962 BM RI 6099,1964); Institution of Fire Engineers (1962, 1972); Madorsky (1964); Risinger (1964a,c,d,h); W.S. Wood (1965); Mansfield (1969); Hilado (1970, 1973); W.B. Howard (1970b); FPA (1971 /14, 15, 1974/22, 1986- CFSD H series NFPA (1972/9, 1990 NFPA 30, 704, 1991/27, 1992 NFPA 49, 325M, 491M, 445); Woinsky (1972); DOT, CG (1974a,b); Rasbash (1975b); Groothuizen and Romijn (1976); Tewarson and Pion (1976); Kletz (1977i); Dokter (1985a); W.J. Bradford (1986a); Clarke (1986b); M.F. Henry (1986); UL (1986 UL 723); Walls (1986); Wharton (1990); BS 476: 1970–.
Calorific value of wood: Goldfinger (1949); A.F. Roberts (1964, 1967b, 1971c); Allan, Cameron and Lambie (1966); Brenden (1967); Hsiang-Cheng Kung and Kalelkar (1973)
Oxygen index: Fenimore and Martin (1966); Abbott (1974)

Solids fires
F.R. Steward (1964, 1971); Kanury and Blackshear (1970); Havens *et al.* (1972); Kanury (1972a–c); Annamali and Durbetaki (1975); W.A. Gray (1979); Vovelle, Mellottee and Delbourgo (1982); Vovelle, Akrich and Delfau (1984); Wichman and Atreya (1987); Wichman and Agrawal (1991); Janssens (1991).

Crib and rack fires
FRS (Fire Res. Note 600); Fons, Clements and George (1963); P.H. Thomas, Simms and Wraight (1964, 1965); P.H. Thomas (1965b); Delichatsios (1976); Hsiang-Cheng Kung (1972); Hsiang-Cheng Kung and Kalelkar (1973); Hsiang-Cheng Kung and Hill (1975–); Emori and Saito (1983); Tewarson (1985); You and Kung (1985); Carrier, Fendell and Wolff (1991); Wolff, Carrier and Fendell (1991)

Free-burning fires, fire plumes
P.H. Thomas (1963); Emmons (1965); B.R. Morton (1965); P.H. Thomas, Baldwin and Heselden (1965); Huffman, Welker and Sliepcevich (1967); Block (1971); S.L. Lee and Otto (1975); G. Cox and Chitty (1980); Heskestad (1981, 1989); Kung and Stavrianidis (1982); Babrauskas (1986a); Zonato *et al.* (1993)
Large area fires: Muraszew, Fedele and Kuby (1979); T.Y. Palmer (1981); Carrier, Fendell and Feldman (1984); R.O. Weber (1989); Heskestad (1991); D.A. Carter (1992); Ghoniem *et al.* (1993); Fendell and Mitchell (1993); Weihs and Small (1993); Husain (1995)
Small area fires: Heikes, Ransohoff and Small (1990)
Subterranean fires: BRE (1989 IP3/98)

Metals fires
Steinberg, Wilson and Benz (1992); Glassman (1993)

Propellant fires
Grumer *et al.* (1961)

Fires in buildings, warehouses
Kawagoe (1958); P.H. Thomas and Heselden (1962); FRS (1963 Fire Res. Tech. Pap. 5, 1966 Fire Res. Tech. Pap. 15, 1975 Fire Res. Note 1029); Kawagoe and Sekine (1963); P.H. Thomas (1963, 1973b, 1981a,b, 1982); P.H. Thomas *et al.* (1963); Roth (1964); Thomas and Hinckley (1964); P.H. Thomas, Simms and Wraight (1964, 1965); FMEC (1967); Waterman (1968); Law (1971, 1991); Langdon-Thomas (1967a,b, 1972); FPA (1970/9, 13, 1971/14, 1973/20, 21, 1982 CFSD FS 6017); P.H. Thomas and Law (1972, 1974); Butler, Martin and Wiersma (1973); BRE (1974 CP 30/74, CP 32/74, CP 43/74, 1978 CP 40/78); Hagglund, Jansson and Onnemark (1974); Rasbash (1974a, 1991); Croce (1975); Fang (1975); HSE (1975 TDN 29); Prahl and Emmons (1975); Quintiere (1975, 1979, 1983); Petterson, Magnusson and Thor (1976); Rockett (1976); Butcher and Parnell (1979); Ove Arup (1977); Theobald (1977); P.H. Thomas and Theobald (1977); Babrauskas and Williamson (1978); Bullen (1978); Quintiere, McCaffrey and Kashiwaga (1978); Bullen and Thomas (1979); Emmons (1979); P.H. Thomas and Bullen (1979/80); Babrauskas (1981, 1986c); D.S. Baker (1981); McCaffrey, Quintiere and Harkleroad (1981); Siu (1982); Drysdale (1985); Lawson and Quintiere (1985); Steckler, Baum and Quintiere (1985); Beyler (1986); Budnick and Evans (1986); Budnick and Walton (1986); Shields and Silcock (1987); Anon. (1988 LPB 84); Ho, Siu and Apostolakis (1988); Jaluria and Kapoor (1988); Rabinkov (1988); Heskestad and Delichatsios (1989); Lockwood and Malalasekera (1989); Peacock and Bukowski (1990); Brandyberry and

Apostolakis (1991a,b); Peacock and Babrauskas (1991); Babrauskas and Peacock (1992); N.R. Marshall and Morgan (1992); McCaughey and Fletcher (1993); Melinek (1993a); Pagella and de Faveri (1993); Chamberlain (1994); Comitis, Glasser and Young (1994).
Warehouses: Barthelemy and Lamboley (1978); Isman (1978); G.T. Atkinson, Jagger and Kirk (1992); D.A. Carter (1992); G.T. Atkinson and Jagger (1994); Christiansen (1994); Smith-Hansen (1994)

Ventilated fires
Tewarson and Steciak (1983); Alvares, Foote and Pagni (1984); Chippett (1984); Mitler (1984)

Smoke
Hilado and Kosola (1977); Rasbash and Drysdale (1982); Fothergill (1984); Marchant (1984); Drysdale (1985); Heskestad (1986); Savilonis and Richards (1988); Gross (1991); Delichatsios (1993a); Ghoniem *et al.* (1993); Kandola and Morris (1994)

Brands from fires
Shao-Lin Lee and Hellman (1969, 1970)

Decomposition products of fires (*see also* Table 18.1)
FRS (1972 Fire Res. Note 913, 947, 951, 1973 Fire Res. Note 966, 1975 Fire Res. Note 1025, 1976 Fire Res. Note 1048); Rasbash (1969b); Hilado (1970, 1973); FPA (1971/14, 1989 CFSD N3); BRE (1974 CP5/74, CP 11/74, CP12/74, CP 91/74, 1976 CP 22/76); Woolley and Raftery (1976); Hilado and Kosola (1977); Chisnall (1978); Einhorn and Grunnet (1978); Hilado, Cumming and Casey (1978); Hilado and Huttlinger (1980, 1981a,b); Herpol and Vandervelde (1981/82); Woolley and Fardell (1982); Landrock (1983); Kaplan and Hartzell (1984); Hartzell, Packham *et al.* (1985); Hartzell, Priest and Switzer (1985); Hartzell, Stacy *et al.* (1985); Alexeeff *et al.* (1986); Delumyea, Moore and Morgan (1986); Doe *et al.* (1986); Pollock, Campbell and Reid (1986); Tsuchiya and Nakaya (1986); Hartzell, Grand and Switzer (1987); M.T. Mills (1987); van Loo and Opschoor (1989); Hartzell (1989); CPD (1992b).
Warehouses: G.T. Atkinson, Jagger and Kirk (1992); D.A. Carter (1992); Smith-Hansen and Jorgensen (1993); G.T. Atkinson and Jagger (1994); Christiansen (1994); Smith-Hansen (1994)

Oil slick fires
Brzustowski and Twardus (1982)

Fires in process plants
H.R. Brown (1956 BM RI 5198); Institution of Fire Engineers (1962); Vervalin (1964a, 1973a); Zabetakis (1965); H.S. Robinson (1968); Hearfield (1970, 1974); FPA (1971/14); Bland and Beddow (1974); Rasbash (1974b); Kletz (1978c, 1979a, 1988d); Kanury (1981); A.F. Roberts (1981/82); Considine, Grint and Holden (1982), BS 5908: 1980.
Cable fires: FPA (1974a); Anon. (1980c); Anon. (1981 LPB 41, p. 5); B.F. Gray *et al.* (1990)
Duct fires: A.F. Roberts and Kennedy (1965); A.F. Roberts, Clough and Blackwell (1966); A.F. Roberts and Clough (1967a,b); de Ris (1970); A.F. Roberts (1971a); Wilde (1972); Church (1978); Lovachev (1978a); Anon. (1979 LPB 30, p. 55); C.K. Lee, Chaiken and Singer (1979); Hunter and Favin (1981); Brandeis and Bergman (1983); Newman and Tewarson (1983); Krupper (1991)
Flange fires: McFarland (1969)
Hydraulic accumulator fires: HSE (SIR 9)
Iron–chlorine fires: Anon. (1991 LPB 98, p. 25)
Lagging fires: P.H. Thomas and Bowes (1961b, 1967); Petkus (1963, 1964); Darling (1967); Lindner and Seibring (1967); Bowes and Langford (1968); Bowes (1974a, 1976); BRE (1974 CP 35/74); Gugan (1974a); Anon. (1977 LPB 17, p. 2); Buch and Filsinger (1985); Britton (1991); Craig (1993 LPB 110)
Pump fires: Kletz (1971); Fromm and Rail (1987b)
Transport: NFPA (1973/10)

Tank fires, including boilover, frothover
Burgoyne and Katan (1947); Burgoyne (1950, 1952); Laney (1963, 1964); Risinger (1964b,f); Herzog (1974); OIA (1974 Loss Inf. Bull. 400–2); Yumoto (1977); Brötz and Schönbucher (1978); Lois and Swithenbank (1979); Viergas, Campos and Oliviera (1984); Broekmann and Schecker (1992); Inamura, Saito and Tagavi (1992); Michaelis, Mavrothalassitis and Pinjeau (1992); Palmer (1992 LPB 106); Purdy, Pitblado and Bagster (1992)
Bitumen tank fires: Anon. (1991 LPB 102, p. 35)

Fires in liquids, leakages and spillages
Rasbash (1956, 1970a); Burgoyne, Roberts and Quinton (1968); Burgoyne and Roberts (1968a,b); Leroy and Johnson (1969); FPA (1971/14); Wilde and Curzon (1971); Stark (1972); A.F. Roberts (1975a); Kletz (1976h); Anon. (1980d,k); Crawley (1982); Toa and Kaviany (1991)

Fire models
Considine (1981); Simpson and Taylor (1984 SRD R276); Drysdale (1985); A.D. Davies (1987); Beard (1992a,b); P.H. Thomas (1992, 1993); Nam and Bill (1993)

Flames
NRC (Appendix 28 *Combustion*); Flamm and Mache (1917); Mache (1918); Bone and Townend (1927); Burke and Schumann (1928a,b); Bone and Newitt (1929); Jahn (1934); B. Lewis and von Elbe (1937, 1938, 1943, 1951, 1961, 1987); Jost (1939, 1946); Forsyth and Garside (1949); Hawthorne, Weddel and Hottel (1949); Hottel (1949, 1953); Hottel and Hawthorne (1949); Scholefield and Garside (1949); G.C. Williams, Hottel and Scurlock (1949); Wohl, Kapp and Gazley (1949); Thring (1952); Gaydon and Wolfhard (1953–); Gerstein (1953); Grove and Walsh (1953); Karlovitz (1953); Karlovitz *et al.* (1953); Wohl (1953); R. Friedman and Burke (1955); Grumer, Harris and Rowe (1956 BM RI 5225); Barnett and Hibbard (1957); Fristrom (1957); Spalding (1957a, 1963a, 1976); Berlad and Yang (1959); van Krevelen and Chermin (1959); Kydd (1959); Prudnikov (1959); Sundukov and Predvoditelev (1959); Zeldovitch and Barenblatt (1959); Westenberg and Favin (1960); Cekalin (1962); Menkes (1962); Potter, Heimel and Butler (1962); Yamazaki and Tsuji (1962); Markstein (1964); Fristrom and Westenberg (1965); Khitrin *et al.* (1965); H. Phillips (1965); Shchelkin and Troshin (1965); Wiebelt (1966); Essenhigh (1967); Gaydon (1967); J.N. Bradley (1969); Edmondson and Heap (1969); Gunther (1969); F. Powell (1969); Hearfield (1970); Emmons (1971); Werthenbach (1971a,b); Fox and Sarkar (1972); Ballal and Lefebvre (1973, 1975c); Chomiak (1973); H.B. Palmer and Beer (1973); Afgan and Beer (1974); Barnes and Fletcher

(1974); R.O. Parker (1974); Eisenberg, Lynch and Breeding (1975); Kanury (1975); Modak (1975, 1978/79); Gugan (1976); Stambuleanu (1976); A. Williams (1976); G. Cox (1977); Glassman (1977); Goodger (1977); Kaptein and Hermance (1977); Lockwood (1977); J.G. Marshall (1977); Lockwood and Syed (1979); Chandra and Davis (1980); Albini (1981); D. Bradley (1982); Buckmaster and Ludford (1982); Ishikawa (1982); Pong Chung and Smith (1982); Jeng, Chen and Feath (1982); W.P. Jones and Whitelaw (1982); S.T. Lee and Tien (1982); Takahashi, Mizomoto and Ikai (1982); F.A. Williams (1982); Heskestad (1983a,b, 1984); Clavin (1984); Ramohalli, Jones and Bashar (1984); Hertzberg (1985); R.S. Levine (1985); Tunc and Venart (1984/5a,b); Zukoski, Cetegen and Kubota (1985); Law (1989); Schefer, Namazian and Kelly (1989); Adiga *et al.* (1990); Carrier *et al.* (1991); Dixon-Lewis (1991); Kennel, Göttgens and Peters (1991); P.H. Thomas (1993)

Premixed flames
Burgess (1962 BM Bull. 604); S.B. Reed (1967, 1971); Vinckier and van Tiggelen (1968); Basu and Bhaduri (1972); N.J. Brown, Fristrom and Sawyer (1974–); Vance and Krier (1974); Lockwood (1977); Strehlow and Savage (1978); Bray, Champion and Libby (1989); Searby (1992); Duclos, Veynante and Poinsot (1993)

Diffusion flames
Wohl, Kapp and Gazley (1949); Barr (1953); H.N. Powell (1955); Sunavala, Hulse and Thring (1957); Schmitz (1967); Bilger (1975, 1976, 1977); Suris, Flankin and Shoring (1977); Kalghatgi (1981–); Chakravarty, Lockwood and Sinicropi (1984); Birch *et al.* (1988); Birch and Hargrave (1989); Delichatsios and Orloff (1989); de Faveri *et al.* (1989); Chao, Law and Tien (1991)
Laminar diffusion flames: Burke and Schumann (1928a,b); Savage (1962)
Turbulent diffusion flames: F.R. Steward (1970); Brzustowski (1973); Kent and Bilger (1973); Chigier and Strokin (1974); Brzustowski, Collahalli and Sullivan (1975); Markstein (1976); Lockwood (1977); Tamanini (1977); Becker and Liang (1978); Becker and Yamazaki (1978); Pergament and Fishburne (1978); Heskestad (1983a); Nguyen and Pope (1984); Bilger (1989); Annaruma, Most and Joulain (1991); D.A. Smith and Cox (1992); Blake and McDonald (1993)
Turbulent jet diffusion flames: Baron (1954); Sunivala, Hulse and Thring (1957); Bilger (1976); Onuma and Ogasawara (1977); Peters and Williams (1983); Kalghatgi (1984); Pitts (1989); Delichatsios (1993b)
Buoyant diffusion flames: P.H. Thomas, Webster and Raftery (1961); Putnam and Grinberg (1965); P.H. Thomas, Baldwin and Heselden (1965); Masliyah and Steward (1969); Steward (1970); Delichatsios and Orloff (1985)
Flame regime intermediate between premixed and diffusion conditions: Talley (1992)

Radiant heat transfer, fire spread
BRE (n.d./2–4, 1974 CP 29/74, CP 72/74); FRS (Appendix 28, F3, F4, Fire Res. Special Rep. 2, 1961 F1, 1963 Fire Res. Tech. Pap. 5, 1966 F6, F8, 1972 Fire Res. Note 921); Lawson and Simms (1952a,b); McAdams (1954); Eckert and Drake (1959); Kreith (1962); Sparrow (1962); Sparrow and Cess (1966, 1978); Law (1969); Hearfield (1970, 1974); FPA (1971/14); Langdon-Thomas (1972); Siegel and Howell (1972, 1991); Sirignano (1972); P.H. Thomas and Law (1972, 1974); Blackshear (1974); L.E. Brown, Wesson and Welker (1974a,b, 1975); Fernandez-Pello and Williams (1974, 1977); W.A. Gray and Muller (1974); Kovacs and Honti (1974); Alpert (1975); Eisenberg, Lynch and Breeding (1975); Feng, Williams and Kassoy (1975); Craven (1976); Groothuizen and Romijn (1976); Klootwijk (1976); Nakakuki (1976); Rasbash (1976c); R.B. Robertson (1976b); Feng and Sirignano (1977); Straitz and O'Leary (1977); Yumoto (1977); HSE (1978b); Modak (1979); D.C. Bull *et al.* (1980); Carrier, Fendell and Feldmann (1980); F.R.S. Clark (1981); Anon. (1984 LPB 56, p. 11); Harmathy (1985); Modest (1993)
Flame radiation: Hottel and Mangelsdorf (1935); Hottel and Smith (1935); Hottel and Egbert (1941, 1942); Daly and Sutherland (1949); Hottel, Williams and Satterfield (1949); Cassel, Liebman and Mock (1957); Foster and McGrath (1960); D.K. Edwards (1963); Siddall and MacGrath (1963); Echigo, Nishiwaki and Hirata (1967); Hottel and Sarofim (1967); R.K. Smith (1967); Tien (1968); Beer and Howarth (1969); Dalzell and Sarofim (1969); Godridge and Hammond (1969); Masliyah and Steward (1969); Sato *et al.* (1969); Dalzell, Williams and Hottel (1970); Leckner (1971, 1972); Lowes and Newall (1971); J.M. Jones and Rosenfeld (1972); Thring and Lowes (1972); Felske and Tien (1973, 1974a,b); C.S. Kelly (1973); N.K. King (1973); Cess (1974); Markstein (1974, 1976, 1977, 1985, 1989); P.B. Taylor and Foster (1974, 1975); C.K. Lee (1975); W.A. Gray, Kilham and Muller (1976); Yuen and Tien (1977); Fishburne and Pergament (1979); Orloff, Modak and Markstein (1979); de Ris (1979); Wagner (1979); Calcote (1981); Ganapathy (1981); Grosshandler and Modak (1981); Orloff (1981); Vervisch, Puechberty and Mohamed (1981); Becker and Liang (1982); Tien and Lee (1982); Coppalle and Vervisch (1983); Frenklach, Taki and Matula (1983); Vervisch and Coppalle (1983); Gill and Olson (1984); Brosmer and Tien (1986); Raparotte and Brzustowski (1986); E.B. Cohen and Taylor (1987); MHAP (1988 LPB 82); Mudan (1989b); Hamins *et al.* (1991); Orloff, de Ris and Delichatsios (1992)
Radiant heat factor: A.F. Roberts (1981/82); Hymes (1983 SRD R275)
Soot: Mie (1908); Arthur and Napier (1955); Schalla and McDonald (1955); Tesner, Robinovitch and Rafalkes (1962); A. Thomas (1962); Yagi and Iino (1962); Bonne, Homann and Wagner (1965); Narasimhan and Foster (1965); Homann (1967); Kunugi and Jinno (1967); McLintock (1968); Fenimore and Jones (1969); J.B. Howard (1969); Columbo and Thring (1972); Feugier (1972); Wersborg, Howard and Williams (1973); Muller-Dethlefs and Schlader (1976); Becker and Yamzaki (1977); Prado *et al.* (1977); Orloff, Modak and Markstein (1979); Wagner (1979); Glassman and Yaccarino (1981); S.C. Lee and Tien (1981); Pong Chung and Smith (1982); Sen and Ludford (1982); Homan (1983); Santoro, Semerjian and Dobbins (1983); Senkan, Robinson and Gupta (1983); Takahashi and Glassman (1984); Hirschler (1985); Kent and Wagner (1985); K.Y. Lee, Zhong and Tien (1985); R.S. Levine (1985); Markstein (1985, 1989); Pagni and Okoh (1985); Santoro and Semerjian (1985); Delumyea *et al.* (1986); Kent and Honnery (1987, 1991);

Glassman (1989); Gülder (1989); McCaffrey and Harkleroad (1989); Megaridis and Dobbins (1989); J.B. Moss (1989); Honnery and Kent (1990, 1992); I.M. Kennedy, Kollman and Chen (1990); Leung, Linstedt and Jones (1991); C.D.Stewart, Syed and Moss (1991); Syed, Stewart and Moss (1991); Fairweather *et al.* (1992); Smedley, Williams and Bartle (1992); Coppalle and Joyeux (1993); Chamberlain (1994)

View factor: Hottel (1930, 1931, 1954); Hamilton and Morgan (1952); McGuire (1953); McAdams (1954); Coulson and Richardson (1955–, 1977–); Rogers and Mayhew (1957); Eckert and Drake (1959); Bird, Stewart and Lightfoot (1960); Chandrasekhar (1960); C.O. Bennett and Myers (1962); Sparrow (1962); Sparrow, Miller and Johnson (1962); Dunkle (1963); Kourganoff (1963); Feingold (1966); Sparrow and Cess (1966, 1978); Hottel and Sarofim (1967); Grier (1969); Rein, Sliepcevich and Welker (1970); Chung and Sumitra (1972); Merriam (1972); Siegel and Howell (1972); Ozisik (1973); Raj and Kalelkar (1974); Minning (1977); Becker (1980a,b); Chung and Naraghi (1981); Howell (1982); Mecklenburgh (1985); Tunc and Venart (1984/85a,b); Crocker and Napier (1986, 1988a,b); Napier and Roopchand (1986); Mudan (1987, 1989b); Wong and Steward (1988); B.C. Davis and Bagster (1989–); Bagster and Davies (1990); Beard *et al.* (1993); CPD (1992a); CCPS (1994/15)

Atmospheric transmissivity: R.O. Parker (1974); Glasstone and Dolan (1980); Horvath (1981); Lihou and Maund (1982); Hymes (1983 SRD R275); Considine (1984 SRD R297); Simpson (1984 SRD R304); Babrauskas (1986b); R.C. Henry (1987); V.C. Marshall (1987); Wayne (1991); CPD (1992a) CCPS (1994/15)

Flames on pools, pool fires

Rasbash (1956); Blinov and Khudiakov (1957); Hottel (1958); Rasbash, Rogowski and Stark (1960); Burgess, Strasser and Grumer (1961); Fons (1961); Magnus (1961); Welker and Sliepcevich (1965, 1966); Agoston (1962); Burgess and Grumer (1962); Burgess and Zabetakis (1962 BM RI 6099); Spalding (1962); P.H. Thomas (1963); P.H. Thomas, Pickard and Wraight (1963); Pipkin and Sliepcevich (1964); Akita and Yumoto (1965); Atallah (1965); Welker, Pipkin and Sliepcevich (1965); Corlett and Fu (1966); A.F. Roberts (1966, 1971b); Corlett (1968, 1970); Glassman and Hansel (1968); Canfield and Russell (1969); Glassman, Hansel and Eklund (1969); Huffman, Welker and Sliepcevich (1969); Masliyah and Steward (1969); B.D. Wood and Blackshear (1969); Hearfield (1970); ICI/RoSPA (1970 IS/74); Murad *et al.* (1970); Akita and Fujiwara (1971); Hillstrom (1971); Torrance (1971); B.D. Wood, Blackshear and Eckert (1971); Yumoto (1971b); Chetty and Voinov (1972); A.R. Hall (1972); de Ris and Orloff (1972); Hertzberg (1973); C.S. Kelly (1973); Nakakuki (1973, 1974a,b, 1976); A.F. Roberts and Quince (1973); Dayan and Tien (1974); Duffy, Gideon and Puttnam (1974); Fu (1974); P. Nash (1974a); Dehn (1975); Escudier (1975); Hirano and Kinoshita (1975); Craven (1976); Dow Chemical Co. (1976); MITI (1976); Brötz, Schönbucher and Schäble (1977); Modak (1977, 1981); Modak and Croce (1977); Yumoto, Takahashi and Handa (1977); Alger *et al.* (1979); NASA (1979); Raj, Moussa and Aravamudan (1979a,b); Anon. (1980d,k); Glassman and Dryer (1980/81); Mizner (1981); Mizner and Eyre (1982); Dinenno (1982); Hsiang-Cheng Kung and Stavrianidis (1982); Kletz (1982h); Moorhouse (1982); Moorhouse and Pritchard (1982); Orloff and de Ris (1982); Pantony and Smith (1982); Sher (1982); Babrauskas (1983, 1986b); Cline and Koenig (1983); Mudan (1984c, 1989b); Santo and Delichatsios (1984); Shinotake, Koda and Akita (1985); Webber (1985 SRD R325); Croce and Mudan (1986); Crocker and Napier (1986); Frank and Moieni (1986); Uguccioni and Messina (1986); Brosmer and Tien (1987); Delichatsios (1987, 1988, 1993a,b); Fischer, Hardouin-Duparc and Grosshandler (1987); Nishio and Machida (1987); Fischer (1988); Koseki and Yumoto (1988); Adiga *et al.* (1989); Bagster and Pitblado (1989); Bouhafid, Vantelon, Soudil *et al.* (1989); Bouhafid, Vantelon, Joulain *et al.* (1989); Fischer and Grosshandler (1989); Koseki (1989); Koseki and Hayasaka (1989); J.B. Moss (1989); Schneider and Kent (1989); Seung Wook Baek and Chan Lee (1989); Arpaci and Selamet (1991); Holen, Brostrom and Magnussen (1991); Koseki and Mulholland (1991); Pineau *et al.* (1991); Ditali, Rovati and Rubino (1992); Hayasaki, Koseki and Toshiro (1992); Inamura, Saito and Tagavi (1992); Klassen *et al.* (1992); Lautkaski (1992); Mangialavori and Rubino (1992); Schonbucher, Gock and Fiala (1992); Cetegen and Ahmed (1993)

LNG fires: HSE/SRD (HSE/SRD/WP 34); Welker, Wesson and Sliepcevich (1969); Hoult (1972a); Atallah and Raj (1973); Fay (1973); May and McQueen (1973); Welker (1973, 1982); Opschoor (1975a,b); Raj and Atallah (1975); Stannard (1977); Raj, Moussa and Aravamulan (1979); Schneider (1980); Blackmore, Eyre and Summers (1982); Ermak, Koopman *et al.* (1982); Mizner and Eyre (1982); Croce, Mudan and Wiersma (1986); Napier and Roopchand (1986); Rosenblatt and Hassig (1986); A.D. Johnson (1992)

LPG fires: Rasbash (1979/80); Blackmore, Eyre and Summers (1982); Mizner and Eyre (1982)

Pool fires on water: A.D. Little (1979); Mizner and Eyre (1983); Arai, Saito and Altenkirch (1990); Alramadhan, Arpaci and Selamet (1991)

Pool fires in enclosures: Tatem *et al.* (1986)

Fires on wicks: Burgoyne, Roberts and Quinton (1968); Toa and Kaviany (1991)

Trench fires

Welker (1965); Alger and Capener (1972); Gollahalli and Sullivan (1974); Mudan and Croce (1984); Croce, Mudan and Wiersma (1986); D.A. Smith (1992)

Fire engulfment, including directed jets

Chichelli and Bonilla (1945–); L.H. Russell and Canfield (1973); C. Anderson *et al.* (1974); Charles (1974); Charles and Norris (1974); Borgnes (1979a,b); Borgnes and Karlsen (1979); Birk and Oosthuize (1982); J.M. Wright and Fryer (1982); Heitner, Trautmanis and Morrissey (1983a,b); Hunt *et al.* (1983 SRD R240); A.F. Roberts, Cutler and Billinge (1983); Solberg and Borgnes (1983); Sousa and Venart (1983); Nylund (1984); Droste *et al.* (1984); Schulz-Forberg, Droste and Charlett (1984); Venart *et al.* (1984); Tunc and Venart (1984/85a); Grolmes and Epstein (1985); Moodie, Billinge and Cutler (1985); Siddle (1986); Aydemir *et al.* (1988); Bainbridge and Keltner (1988); Beynon *et al.* (1988); Birk (1988, 1989); Droste and Schoen (1988); Moodie (1988); Moodie *et al.* (1988); Ramskill (1988); Venart *et al.* (1988); Venart *et al.* (1989); Dancer (1990);

Hadjisophocleous, Sousa and Venart (1990); Tanaka *et al.* (1990); Bennet *et al.* (1991); Cowley and Pritchard (1991); Crespo *et al.* (1991); Verheif and Duijm (1991); Giselle and Krause (1992); Hernandez and Crespo (1992); Duijm (1994)

Fireballs, BLEVEs (*see also* Table 17.36)
Gayle and Bransford (1965); van Nice and Carpenter (1965); R.W. High (1968); Bader, Donaldson and Hardee (1971); Patterson *et al.* (1972); Hardee and Lee (1973, 1975, 1977–78); MITI (1976); Fay and Lewis (1977); Hasegawa and Sato (1977, 1978); V.C. Marshall (1977a, 1987); Maurer *et al.* (1977); Hardee, Lee and Benedick (1978); HSE (1978b, 1981a); A. Baker (1979); Fay, Desgroseillers and Lewis (1979); Harvey (1979b); R.C. Reid (1979); Appleyard (1980); Gillette (1980); Mallory (1980); Aravamudan and Desgroseillers (1981); Kletz (1981n); A.F. Roberts (1981a,b, 1981/82, 1982); Considine, Grint and Holden (1982); Crawley (1982); Moorhouse and Pritchard (1982); Williamson and Mann (1981); Lihou and Maund (1982); Pantony and Smith (1982); Ursenbach (1983); Martinsen (1984); D.L.M. Hunt and Ramskill (1985); Köhler (1985); Pietersen (1985); Tunc and Venart (1984/5a,b); Blything (1986); Hirst (1986); Roper *et al.* (1986); Bagster and Pitblado (1989); J.B. Moss (1989); Buckmaster, Joulin and Ronney (1991); Pineau *et al.* (1991); Satyanarayana, Borah and Rao (1991); Buckmaster, Gessman and Ronney (1992); Buckmaster and Joulin (1993); Buckmaster, Smooke and Giovangigli (1993); Prugh (1994)

Vapour cloud fires, flash fires
Kletz (1971); Eisenberg, Lynch and Breeding (1975); Fay and Lewis (1975, 1977); Raj and Emmons (1975); A.D. Little (1979); Hogan (1982); Rodean *et al.* (1984); Roper, Arno and Jaggers (1991); Seshadri, Berlad and Tangirala (1992); CCPS (1994/15)

Jet flames
Hawthorne, Weddell and Hottel (1949); Hottel and Hawthorne (1949); Hottel (1953); Thring and Newby (1953); Goldburg and Sin-I Cheng (1965); Chervinsky and Manheimer-Timnat (1969); Hoehne, Luce and Miga (1970); Guruz *et al.* (1974); Lockwood and Naguib (1975); Becker and Yamazaki (1978); Becker (1980a,b); Kalghatgi (1983); Peters and Williams (1983); Hirst (1984, 1986); Sonju and Hustad (1984); Tunc and Venart (1984/85b); Delichatsios and Orloff (1985); de Faveri *et al.* (1985); Hustad and Sonju (1986); McCaffrery and Evans (1986); M.T.E. Smith *et al.* (1986); Beychok (1987b); Chamberlain (1987, 1989); D.K. Cook, Fairweather, Hammonds and Hughes (1987); D.K. Cook, Fairweather, Hammonds and O'Brien (1987); Delichatsios (1987, 1993a); Leahey and Schroeder (1987); Crocker and Napier (1988b); Bagster and Pitblado (1989); Birch *et al.* (1989); Greenberg (1989); Grint (1989); Loing and Yip (1989); J.B. Moss (1989); Mudan (1989b); Tam and Cowley (1989); Turns and Lovett (1989); J. Cook, Bahrami and Whitehouse (1990); Damiano (1990); R.W. Davis *et al.* (1990); D.A. Carter (1991); D.K. Cook (1991a); Cowley and Pritchard (1991); Fairweather *et al.* (1991); Peters and Göttgens (1991); Arnaud *et al.* (1992); Fairweather, Jones and Linstedt (1992); Gollahalle, Khanna and Prabhu (1992); Villermaux and Durox (1992); API (1990 RP 521); Coppalle and Joyeux (1993); Sivathanu and Gore (1993); Duijm (1994); A.D. Johnson, Brightwell and Carsley (1994); C.R. Kaplan *et al.* (1994)

Mist and spray fires
Godsave (1953); Burgoyne and Cohen (1954); J.A. Browning and Krall (1955); Hottel, Williams and Simpson (1955); Kobayasi (1955); Agoston, Wise and Rosser (1957); Bolt and Saad (1957); J.A. Browning, Tyler and Krall (1957); Fraser (1957); Kumagai (1957); F.A. Williams (1959); Reichenbach, Squires and Penner (1962); Rosser (1967); Aldred and Williams (1966); Eisenklam and Arunachalam (1966); Eisenklam, Arunachalam and Weston (1967); Faeth (1967, 1977, 1979, 1983); Polymeropoulos and Peskin (1969); Sioui and Roblee (1969); Lemott, Peskin and Levine (1971); Law and Williams (1972); Mizutani and Nakajima (1973); A. Williams (1973, 1976, 1990); Polymeropoulos (1974, 1984); Kapila, Ludford and Buckmaster (1975); Hayashi and Kumagai (1975); Law (1975); Miyasaki and Mizutani (1975); Polymeropoulos and Das (1975); Yuen and Chen (1976); Sangiovanni and Kesten (1977); Ballal and Lefebvre (1978, 1979, 1981a,b, 1983a,b); Anon. (1980h); Briffa (1981); K.N. Palmer (1983); Yule, Ereaut and Ungut (1983); Pindera and Brzustowski (1984); Sichel and Palinaswamy (1985); Polymeropoulos and Peskin (1989); P.J. Bowen and Shirvill (1994a,b)

Flames on flares
Ludwig *et al.* (1968); Becker (1980a,b); de Faveri *et al.* (1985); Beychok (1987b); Chamberlain (1987); D.K. Cook, Fairweather, Hammonds and Hughes (1987); D.K. Cook, Fairweather, Hankinson and O'Brien (1987); A.D. Johnson, Brightwell and Carsley (1994)

Flames on pipelines
Hoff (1983); Hirst (1984); Chamberlain (1987); D.A. Carter (1991)

Effect of fire on materials, buildings
Kashiwagi (1974, 1976, 1979a,b, 1981); C.S. Kelley (1975); Hymes (1984); J.L. Bryan (1986); Rasbash, Drysdale and Deepak (1986); van Loo and Opschoor (1989); Opschoor, van Loo and Pasman (1992)
Ignition and combustion of wood, cellulose: Bamford, Crank and Malan (1946); Hopkins (1952); E.K. Lawrence (1952); Lawson and Simms (1952a,b); Stout (1952); Gardon (1953, 1959); C.C. Williams (1953); Hottel and Williams (1955); S. Martin (1956, 1964, 1965); Akita (1959); Simms (1960, 1961, 1962, 1963); Courteney (1962); A.F. Roberts and Clough (1963); Blackshear and Murty (1965); Weatherford and Sheppard (1965); Lipska (1966); Weatherford and Valtierra (1966); Koohyar (1967); Murty and Blackshear (1967); A.F. Roberts (1967a, 1971d); Simms and Law (1967); Rasbash and Langford (1968); Deverall and Lai (1969); Kosdon, Williams and Buman (1969); A.F. Roberts (1970); W.K. Smith and King (1970); Wesson (1970); Alvares and Martin (1971); Garg and Steward (1971); Panton and Rittmann (1971); Wesson, Welker and Sliepcevich (1971); Kanury (1972a–c); Kashiwagi (1974, 1979a,b, 1980, 1981); Ndubizu and Durbetaki (1978); EPRI (1979b, 1981a); Gelderblom (1980); Vovelle, Mellotée and Delbourgo (1982); Yoshizawa and Kubota (1982); Cullis *et al.* (1983a,b); Wichman and Atreya (1987); Janssens (1991)
Ignition of flammable liquids: Burgoyne and Roberts (1968a); Burgoyne, Roberts and Quinton (1968);

Sirignano and Glassman (1970); A.F. Roberts and Quince (1973); Kashiwagi (1980); Dorofeev *et al.* (1993)

Flame spread
Kinbari, Endo and Sega (1966); Baldwin (1968); de Ris (1969); Magee and McAlevy (1971); Kanury (1972a); W.J. Parker (1972); Akita (1973); Fernandez-Pello and Williams (1974, 1977); Hirano, Noreikis and Waterman (1974); Alvares (1975); Kashiwagi (1976); Fernandez-Pello (1977a,b, 1984); R. Friedman (1977); F.A. Williams (1977); Hirano and Tazawa (1978); Annamalai and Sibulkin (1979a,b); Fernandez-Pello and Mao (1981); Quintiere (1981); Fernandez-Pello and Hirano (1983); Ray and Glassman (1983); Anon. (1984 LPB 56, p. 11); Alpert and Ward (1984); Delichatsios (1985); Drysdale (1985); Takeno and Hirano (1989); Mekki *et al.* (1991); Mitler (1991); Drysdale and Macmillan (1992); Hirano and Sato (1993)
Flame spread over liquids: Sirignano and Glassman (1970); Drysdale (1985); Burgoyne and Roberts (1968a,b); Burgoyne, Roberts and Quinton (1968); MacKinven, Hensel and Glassman (1970); Welker, Wesson and Sliepkevich (1971); Torrance and Mahajan (1975); Suzuki and Hirano (1982); Murphy (1985); Hirano and Suzuki (1993)
Flame spread over oil-soaked ground: Ishida (1986, 1988, 1992)

Effect of fire on people
Williams *et al.* (n.d.); Bigelow *et al.* (1945); Henriques (1947); Moritz and Henriques (1947); J.P. Bull and Squire (1949); Buettner (1950, 1951a,b, 1952, 1957); Hardy, Wolff and Goodell (1952); Benjamin (1953); Elder and Strong (1953); Hardy, Jacobs and Meixner (1953); J.P. Bull and Fisher (1954); Hinshaw (1957); Stoll and Greene (1958, 1959); Mixter (1959); Glasstone (1962); Mehta and Wong (1967); Schlapowksy (1967); Stoll and Chianta (1969, 1971); Graves (1970); J.P. Bull (1971); White (1971); Arnold *et al.* (1973); Denison and Tonkins (1967); Mehta, Wong and Williams (1973); Wulff (1973); Wulff *et al.* (1973); I.F.K. Muir and Barclay (1974); Wulff and Durbetaki (1974); Eisenberg, Lynch and Breeding (1975); Lawson and Rasbash (1976); Hardee and Lee (1977/78); Seader and Einhorn (1977); Einhorn and Grunnet (1978); HSE (1978b, 1981a); Artz, Moncrief and Pruit (1979); Carson (1981); Pantony (1981); Williamson and Mann (1981); Crawley (1982); J.W.L. Davies (1982); Hummell (1982); Mecklenburgh (1982, 1985); Anon. (1983e); Hymes (1983 SRD R275, 1984); Kemble (1983); Pietersen (1985); Sutherland (1985); J.L. Bryan (1986); W. Clark and Fromm (1987); Goldin (1987); J.C. Lawrence and Bull (1988); Mudan (1989b); API (1990 RP 521); Boydell (1990 SRD R536); McCarthy (1990); Salisbury (1990); J.C. Lawrence (1991); Pineau *et al.* (1991); CPD (1992b); Opschoor, van Loo and Pasman (1992); CCPS (1994/15); Lees (1994a); Shoemaker (1995)
BS 5980: 1980

Hazard assessment
ASTM (1982 STP 762); Budnick (1986); F.B. Clarke (1986a); J.R. Hall (1986); Milke (1986); J.M. Watts (1986); H.E. Nelson (1987); MHAP (1988 LPB 82); FPA (1990 CFSD FPDG 7); Ramachandran (1990c); J.R. Hall and Sekizawa (1991); G.T. Atkinson, Jagger and Kirk (1992); Melinek (1993c); Williamson and Dembsey (1993)

Table 16.2 *Selected references on fire prevention, protection and control*

FIA (n.d.); FPA (Appendix 28, CFSD OR series, 1964/2, 1965/3, 1968/5, 1969/7, 8, 1971/14, 1972/18, 1974/26, 1975 S10, 1979 CFSD FS 6013, 1988 CFDS GP5, 1989 CFSD FS 6011, FS 6012, 1990 CFSD FS 6014); FRS (Appendix 28, 1973 Fire Res. Note 963); IRI (n.d./1, 2, 4, 1964/5, 1966/7); MCA (SG-13, SG-17); NFPA (Appendix 27, 28, 1976/17, 1980/19, 1986/19, 1988/21, 22, 1989/23, 24, 1990/26, 1991/27, 1992 NFPA 1); NRC (Appendix 28 *Fire, Fire Protection*); UL (Appendix 27); Ashton (1961); Bahme (1961); Risinger (1962); Vervalin (1962, 1964a, 1966, 1972a, 1973a,g, 1975a, 1985a); R.V.Wright (1962); Bateman (1963); Webb (1963); Bluhm (1964a); Lindemann and Whitehorn (1965); Dow Chemical Co. (1964, 1966a,b, 1976, 1980, 1987, 1994); FMEC (1967); Aubrecht, Lindemann and Schreiber (1968); BCISC (1968/7); Leeah (1968); P. Nash (1969); Newall (1969); Rasbash (1969a, 1970b, 1974a,b, 1976a, 1977a, 1980a,c); Watkins (1969); Way (1969); Hearfield (1970); HSE (1970 HSW Bklt 10); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74, 1975 IS/107); Constance (1971a); Klaassen (1971); Kletz (1971, 1972a, 1974e, 1975d); Strother-Smith (1971); Underwood (1971–); Birchler (1972); Lockwood (1973a); Ackroyd (1974); Emmons (1974, 1990); Home Office (1974– *Manual of Firemanship*); Hoy-Petersen (1974); R.B. Robertson (1974a,b, 1976a,b); Unwin, Robins and Page (1974); Drewitt (1975); PITB (1975/6); Clayton (1976); J.M. Rees (1976); Spiers (1976); ASTM (1977 STP 614, 1985 STP 882); N.T. Freeman (1977); Monroy and Majul (1977); H.West and Brown (1977); Coleman (1978); Beard (1979); R. King and Magid (1979); Planer (1979); IP (1980 Eur. MCSP Pt 2, 1981 MCSP Pt 1, 1987 MCSP Pt 9, 1993 MCSP Pt 19); Anon. (1981q); Beaumont (1981); Chandnani (1981); Hilado and Huttlinger (1981a); Anon. (1982 LPB 43, p. 1); Benedetti (1982); W.S. Wood (1982a); Anon. (1983d); Besnard (1983); R.S. Levine and Pagni (1983); New (1983); API (1984 RP 2001, 1991 RP 2003); British Gas (1984 BGC/PS/SFP1); Prugh (1985–); Soden (1985); Cote (1986); Cote and Linville (1986); Haessler (1986); Anon. (1987 LPB 74, p. 17); Burke and Finucane (1988 SRD R428); Quintiere (1988); Ramachandran (1988); Haverstad (1989); Hirst (1989); NSW Government (1989a); Pastorini *et al.* (1989); Tuhtar (1989); Barnfield and Hay (1990); Ellinor (1990); Renowden and Woolhead (1990); Becker and Hertel (1991); Clerehugh (1991); Hirano (1993); C.J. King (1993); Shelley (1993)
BS (Appendix 27 *Fire Protection*)

Fire risk management
FPA (CFSD MR series); ASTM (1982 STP 762); NFPA (1986 NFPA 550); Alexander (1992b); C.J. King and Alexander (1992); C.J. King (1993)

Buildings
BRE (Appendix 28, 1974 CP 72/74, 1975 CP 37/75); FPA (n.d., CFSD B and CFSD series, 1971/14, 1973/20, 21, 1974/24); FRS (Appendix 28); Langdon-Thomas (1967a,b, 1972); Dahms (1964); ASTM (1967, 1979 STP 685); ISO (1968); Cutmore (1972); Malhotra (1972, 1977, 1984a,b); Binns, Nelson and Thompson (1973); G.M.E. Cooke (1974, 1975); ASCE (1975/4); Harmathy (1977); Raes (1977); Quintiere, Macaffrey and Kashiwagi (1978);

Lecornu (1980); BRE (1982 IP22/82, 1984 IP15/84, 1989 IP21/89); Drysdale (1985); Kendik (1986); Shields and Silcock (1987); Gross (1991); BS 476: 1970, BS 5306: 1976–, BS 5588: 1978–

Time–temperature curves: Hinkley (1984); Shipp (1984); Harmathy and Sultan (1988)

Fire resistance: Ministry of Works (1946); BRE (1975 CP37/75); Home Office (1975 Manual of Firemanship Bk 8); Janss and Minne (1981/82); Malhotra (1984a,b); Gehri (1985); Odeen (1985); K.J. Schwartz and Lie (1985); American Insurance Services Group (1986); Anchor, Malhotra and Parkiss (1986); Jacobsen (1986); UL (1986 UL 263); Choi (1987); Cullington (1987); Harmathy and Oleskiewicz (1987); Harmathy and Sultan (1988); Pettersson (1988); NFPA (1990 NFPA 251, 262, 1989 NFPA 258, 1992 NFPA 220, 1992/29, 1993 NFPA 80A, 259); G. Butcher (1991); Hosser, Dorn and Richter (1994)

Fire resistance of steel: FPA (n.d.); FRS (1966 Fire Res. Tech. Paper 15); UL (1981 UL 1709); Klingsch (1981/82); Wickström (1981/82); Witteveen and Twilt (1981/82); American Iron and Steel Constructors (1983); European Convention for Constructional Steelwork (1985); Wickstrom (1985); Barnfield (1986); Franssen and Bruls (1986); Anderberg (1988); G.M.E. Cooke (1988); Gandhi (1988); Kirby and Preston (1988); Rubert and Schaumann (1988); Twilt (1988); Melinek (1989); Schneider (1990); Burgess, Olawale and Plannk (1992); Franssen and Dotreppe (1992); Tomecek and Milke (1993)

Fire resistance of concrete: Schneider (1988); O'Meagher and Bennetts (1991); Sullivan and Sharshan (1992)

Fire resistance of glass: FPA (CFSD B series); Howe (1989); Klein (1990); Jackman (1993); Joshi and Pagni (1994)

Oil soaked floors: FPA (1973 S4, 1983 CFSD GP 10)

Piped services: FPA (1973/21, 1982 CFSD FS 6017)

Fire ventilation, smoke control: ASHRAE (n.d./1); IRI (n.d./3); FRS (1964 Fire Res. Tech. Pap. 10, 1965 F5); Leach and Bloomfield (1973, 1974 BRE CP 36/74); Gerhardt (1982); BRE (1984 IP21/84, IP22/84); Marchant (1984); Drysdale (1985); Hinkley (1986); NFPA (1988 NFPA 92A, 1991 NFPA 92B); FPA (1989 CFSD FS 6018, 1990 CFSD FRDG 3); Wighus and Medland (1989); Wild (1989)

Fire venting and sprinklers: Naidus (1981a); Heselden (1982); Holt (1982); Hinkley *et al.* (1992)

Doors: FPA (CFSD FPDG 14, 1974/24, 1990 CFSD GP 11); NFPA (1990 NFPA 80)

Fire dampers: Baines (1988 LPB 84); UL (1989 555); Cullen (1990)

Emergency lighting: C. Watts (1984); BS 5266: 1981–

Handling of flammable materials

MCA (SG-3); Bahme (1961, 1972); FPA (1964/1, 1970/12, 1971/14, 1974 S5, 1987 CFSD FS 6028); Orey (1973); NFPA (1972/9, 1990 NFPA 30, 1991 NFPA 49, 325M, 491M, 1991/27); HSE (1978 HS(G) 3); Bradford (1986b)

Handling cylinders: Carver *et al.* (1977); CGA (1983 SB-3, 1985 SB-10, 1990 P-1, SB-4)

Plant layout (*see also* Table 10.2)

Landy (1964a–c); Seppa (1964); FPA (1971/14); Hearfield (1970); Atallah and Allan (1971); Simpson (1971); Day and Moorhouse (1973); Mecklenburgh (1973, 1976, 1982, 1985); R.B. Robertson (1974a,b, 1976a,b); Klootwijk (1976); Anon. (1982j); Martinsen, Johnson and Millsap (1989); Gore Willse and Smith (1993)

Warehouses

FPA (1970/9, 13, 1972/17, 19); FRS (1972 Fire Res. Note 914, 916, 944, 1977 Fire Res. Note 1068); P. Nash (1972a, 1977a); BRE (1974 CP 68/74, 1988 IP5/88); Home Office (1974/10); Bridge (1977); R.A. Young and Nash (1977); Parnell (1979); Anon. (1980t); Baldovinetti (1983); Field (1985); Mackintosh (1988 LPB 84); Murrell (1988); Johnston (1989 LPB 85); Palmer (1989 LPB 86); Murrell and Field (1990); NFPA (1991 NFPA 231C)

Electrical protection, hazardous area classifiication

ICI (n.d.a); IEC (n.d.); Illuminating Engineering Society (n.d.); IEE (1971 Conf. Publ. 74, 1975 Conf. Publ. 134, 1982 Conf. Publ. 218, Control Ser. 17, 1988 Conf. Publ. 296); MCA (SG-19); Post Office (n.d.); SMRE (Elec. Hazards 1–7); Swann (1957, 1959); EEUA (1959 Doc. 9, 1969 Doc. 32); R.W. Scott (1961, 1964); IRI (1965/6); R.Y. Levine (1965a,b, 1968a,b, 1972a, 1983); Magison (1966, 1975, 1978); Burgoyne (1967b, 1969, 1971); ICI/RoSPA (1970 IS/74, 1972 IS/91); Arnaud (1971); Bartels (1971a, 1975a,c, 1977–); Bartels and Howes (1971); Cockram (1971); W. Cooper (1971); Cowen, Godsmark and Goodwin (1971); Dreier and Engel (1971); FPA (1971/14); Gehm and Bittner (1971); Heidelberg (1971); Lord (1971); MacCarthy (1971); J. Nixon (1971); Palles-Clark and James (1971); Steen (1971); Wheatley (1971); Short (1972, 1982, 1985); API (1973 RP 500B, 1982 RP 500A, 1984 RP 500C, 1991 RP 500); Schön (1973, 1977); Arnaud and Jordan (1975); Bartels and Day (1975); Buschart (1975); Chubb, Pollard and Butterworth (1975); Ellis (1975); N.C. Harris (1975); Nailen (1975); Rogowski (1975); Towle (1975a); Rees (1976); IBC (1981/9, 1991/81); Marshall (1981 LPB 39); J.T. Woods (1981); D.R. Brown and Gregory (1982); Bryce, Ramsey and Seaton (1982); B.D. Cooper (1982); Gwyther (1982); Hay (1982); O'Shea (1982, 1985); Palles-Clark (1982); Peck and Palles-Clark (1982); Shevchenko *et al.* (1982); Summers-Smith (1982); British Gas (1983 BGC/PS/DAT12, 1986 BGC/PS/SHA1); Boon (1983); Bryce and Robertson (1983); Calder and Magison (1983); Joshi (1983); ISA (1984 S12.12, 1987 RP 12.6, 1988 S12.10); Pankowski (1984); Mecklenburgh (1985, 1986); Ashmore (1987a,b); IMechE (1987/92); H. Kramer (1987); NFPA (1988/20, 1991 NFPA 497B, 497M, 1992 NFPA 497A, 1993 NFPA 70, 1993/35); A.W. Cox, Lees and Ang (1990); IP (1990 MCSP Pt 15, 1991 MCSP Pt 1); Ahern (1991); AGA (1992/17); BS (Appendix 27 *Hazardous Area Classification*), BS 4683: 1971–, BS 5345: 1977–, BS 5501: 1977–

Dusts: ICI/RoSPA (1972 IS/91); EEUA (1973 Doc. 47D)

Safeguarding: EECS (SFA 3009, 1992 EECG2); Riddlestone (1967, 1975, 1979); Engel and Wickboldt (1975); Macmillan (1975, 1982); HSE (1984 HS(G) 22)

Flameproofing, explosion proofing

Ministry of Power (n.d.a); NCB (n.d.a); SMRE (Elec. Hazards 2, 3, 7); Underwriters Laboratories (1951); IEE (1962 Conf. Publ. 3); Gelfer *et al.* (1964); Northrup (1964); Carhart (1968); House (1968a); Bartels (1971b, 1975b); Eastwood (1971); H. Phillips (1971a,b, 1972b,

1973, 1984); Lunn and Phillips (1973); Davison and Lord (1974); Fleisig (1975); Maekawa (1975); Sansom and Gust (1975); Maekawa, Takeichi and Kato (1978); Maekawa and Takeichi (1979); Shevchenko *et al.* (1982); Cleare (1991)
BS 229: 1957; BS 4683: 1971; BS 5501: Pt 5: 1977; BS 5345: Pt 3: 1979

Intrinsic safety
BASEEFA (SFA 3012, 1970 SFA 3004); EECS (SFA 3012); Ministry of Power (n.d.b); NCB (n.d.b); SMRE (Elec. Hazards 1, 1968 Res. Rep. 256); Barlow (1963); Burgoyne (1965c); Hickes (1968, 1969, 1972); Redding (1969, 1971a,b, 1972); A.E. Turner (1969); Weismantel (1969b); Cartwright and Widginton (1971); Hickes and Brown (1971); Kheradmand-Fard (1971); Deloney (1972); Deuschle and Tiffany (1973); Krigman and Redding (1974); Weatherhead (1977); Hutcheon (1981); Calder (1982); Garside (1982); Bartels (1983); Bass (1984); Magison (1984); Beevers (1986); Tortoishell (1986); ISA (1987 RP 12.6)
BS 5345: Pt 4: 1977; BS 5501: Pt 7: 1977; BS 5501: Pt 9: 1982

Purging, pressurization
ICI/RoSPA (1972 IS/91); Ecker, James and Toensing (1974); Hinds (1975); Rogerson (1982); E.G. Butcher and Moss (1991); C. Campbell (1991–); NFPA (1993 NFPA 496)
BS 5501: Pt 3: 1977; BS 5345: Pt 5: 1983

Instrumentation
Magison (1966, 1975, 1978, 1984); Redding (1971a,b, 1972, 1975); Towle (1975b); Bossert (1976); Foxboro Co. (1980); Hutcheon (1981); Garside (1982); Macmillan (1982); Corrigan (1990)

Portable apparatus
EEUA (1958 Doc.4); IGasE (1970/9); UL (1992 UL 781)

Diesels
Lloyds Register (n.d.); HSE (1977g); ICI (1977); Oil Companies Materials Association (1977); BP Trading Ltd (1980); EEMUA (1983 Publ. 107)

Electrical surface heating
ICI/RoSPA (1972 IS/91); Angel (1975); Dobie, Cunningham and Reid (1976); UL (1990 UL 130)

Inerting
Hotchkiss and Weber (1953); P.A.F. White and Smith (1962); Funk (1963); Husa (1964); Penland (1967); Rosenberg (1968); H.A. Price and McAllister (1970); Kletz (1971, 1984 LPB 56); Kurz (1973); Loeb (1974); Craven (1975); Gammell (1976); Simon (1976); Corlett, Stone and Williams (1980); Polytechnic Inst. (1980); Schwarz (1980); Depaola and Messina (1984); Halpern, Nyce and Wrenn (1986); Wrenn (1986); Tufano (1992)

Lightning protection
Baatz (1977); Golde (1977a,b); Gumley, Invernizzo and Khaled (1977); Rusck (1977); Saraoja (1977); FMEC (1987 LPB 73); UL (1988 UL 96)

Jet flame protection
Ranz and Marshall (1952); Yuen and Chen (1978); van der Schaaf (1986); Lev (1991); Shirvill (1992)

Fire detection and alarm
FPA (1971/14, 1989 CFSD PE 1, 1991 CFSD FPDG 6); FRS (1970 Fire Res. Note 810, 1971 Fire Res. Note 899, 1972 Fire Res. Note 932, 1974 Fire Res. Symp. 6, 1977 Fire Res. Note 1063); Rasbash (1972); J.L. Bryan (1974); M.J. Miller (1974); BRE (1975 CP 29/75, CP 32/75); Haessler (1975); NFPA (1975/14, 1990 NFPA 72E, 1993/36, 1994/38); P. Nash and Theobald (1976a,b); Benarie (1977); R.G. Bright (1977); Rutstein (1979a); Anon. (1980g); Street, Williams and Alexander (1980); Cullis and Firth (1981); R. Phillips (1981); Bearman (1983); Frost (1983); R.W. Murray and O'Neill (1983); Scheidweiler (1983); von Tomkewitsch (1983); Finucane (1984 LPB 59); Gupta (1985); Gupta and Dharmadhikari (1985); Musselwhite (1985); O'Shea (1985); Todd (1985); Vaughn (1986); Atallah and Guzman (1987); Combley (1987); Northey (1988); Bellamy (1989); Drake (1989); Medlam (1990); Ramachandran (1991)
Gas, smoke and fire detectors: BASEEFA (SFA 3007); SMRE (Gas Detectors 1–11); UL (Appendix 27, 1985 UL 217, 268A, 1987 UL 521, 1988 UL 268); Schall (1962); R.L. Swift (1963); Steel (1971); FRS (1972 Fire Res. Note 938, 1973 Fire Res. Note 957); Firth, Jones and Jones (1973, 1974); HSE (1973 TDN 45, 1980 EC 3, EC 4, 1987 CS 1); Smith (1973); Steen (1973); Verdin (1973); Bossart (1974); Johanson (1974, 1976); Allan and Schiff (1975); Associated Octel Co. (1975 Bull. 13); Riley (1975); Anon. (1976l); BRE (1976 CP 50/76); Dailey (1976); Herrick (1976); P. Nash and Theobald (1976a,b); K.N. Palmer (1976a,c); Weiby and Dickinson (1976); Anon. (1977h); Kletz (1977i); Gowar (1978); Kunz znd Thalman (1978); St John (1978); Anon. (1979f,g); Bond (1979); H.N. Nelson (1979); Schaeffer (1980); Snee (1980); Cullis and Firth (1981); Mannon (1981); C. Martin (1981); Boccio (1982); Sonley (1982); Heitman (1983); Middleton (1983); Ricca (1983); Beyler (1984); Larsen (1984); British Gas (1986 Comm. 1298); ISA (1986 S12.13.1, 1987 RP 12.13 Pt II); Penny (1986); Anon. (1987m,x); EEMUA (1988 Publ. 155); Cholin (1989a,b); Grover (1990); Mowrer (1990); NFPA (1990 NPFA 72E); API (1991 Publ. 2031); Ishii *et al.* (1991); Okayama (1991); Ramachandran (1991); A.J. Rogers (1991); Smithies, Burry and Spearpoint (1991); Björkman, Kokkala and Ahola (1992); Buckland (1992); Varey (1992a); Willey (1992); BS (Appendix 27 EN series), BS 5445: 1977–
Fire alarm: Fire Offices Committee (n.d.b); EEUA (1972 Doc. 45D, 1975 Doc. 46D)

Fire insulation, fireproofing
Steverding and Nieberlein (1965); Waldman (1967); Way and Hilado (1968); Boult, Gamadia and Napier (1972); Boult and Napier (1972); Heselden, Theobald and Bedford (1972); Law (1972, 1991); Castle (1974); Cooke (1974, 1975, 1988); Feldman (1974); Kayser (1974); McMillan (1974); Montle and Mayhan (1974); O'Rourke (1974); Schwab and Lawler (1974); Hildenbrand (1975); Rains (1975, 1977); Warren and Corona (1975); Klootwijk (1976); Florence (1977); Kawaller (1977, 1980); Castle

(1979); Anon. (1980 LPB 31, p. 5); Modak and Orloff (1980); Melinek (1989); Barry (1991); Shirvill (1992)
Fire resistance: SMRE (Fire 1, 6); Parnell (1977); Duffy (1983); Corona (1984); Berhinig (1985); Buck and Belason (1985); Dilliberto and Gratzol (1985); Rains (1985); Gustaferro and Lin (1986); Castle and Castle (1987); Lathom, Kirby and Thomson (1987); Melinek and Thomas (1987); API (1988 Publ. 2218)
Intumescent coatings, seals: O'Rourke (1974); R. James (1988); Gillon (1989); Droste (1992); Hulin (1993)

Fire water systems
L.T. Wright (1962, 1964); R. Wilson (1964a,b); FPA (1971/14, 1988 PE 7, 1989 PE 8, 1990 PE 6); Orey (1972c); Sylvia (1972b,c); W.S. Thompson (1972, 1973); FRS (1973 Fire Res. Note 959); Woodard (1973); R.B. Robertson (1974a,b, 1976a,b); Unwin, Robins and Page (1974); Klootwijk (1976); Theobald (1981, 1984); Hodge (1985); Hodnett (1986d); NFPA (1988 NFPA 291, 1989 NFPA 14A, 1992 NFPA 1961, 1993 NFPA 14, 1962, 1963)
Fire pumps: UL (1988 UL 1478; 1991 UL 1247); NFPA (1990 NFPA 20)
BS 5041: 1974–; BS 5306: 1976–; BS 750: 1984; BS 5908: 1990

Water sprinklers and sprays
FPA (PE 10, 1970/11, 1971/14, 1985 PE 13, 1989 PE 9, 11, 12); Nickerson (1954); Rasbash and Rogowski (1957); Rasbash and Stark (1960, 1962); Rasbash, Rogowski and Stark (1960); C.M. Wood (1961); Rasbash (1962); NFPA (1964/3, 1975/15, 1987 NFPA 13A, 1990 NFPA 15, 17A, 18, 1990/25, 1991 NFPA 13, 1994/37, 39); Chaillot (1966); O'Dogherty, Nash and Young (1966); FMEC (1967); Fire Offices Committee (1968); Charney (1969); FRS (1971 Fire Res. Note 899, 1972 Fire Res. Notes 914, 916, 1974 Fire Res. Note 1003); Kalelkar (1971); Association Nationale pour la Protection contre l'Incendie (1972); P. Nash (1972a, 1973a, 1974a,b, 1975a,b, 1976, 1990); W.S. Thompson (1972, 1973); Arscott, Street and Twamley (1973); Bray (1973, 1980); BRE (1975 CP 29/75, CP 42/75, CP 67/75, CP 77/75, CP 78/75, CP 79/75, 1976 CP 52/76, 1977 CP 9/77); Leworthy (1975); P. Nash and Theobald (1976a,b, 1976 BRE CP 50/76, 1988 IP5/88); P. Nash and Young (1976); Tamanini (1976); Beyler (1977); FMEC (1977, 1986 LPB 71); Ashfield (1979, 1993); Hems (1979, 1983); Rieschl (1979); Anon. (1980t); Barris and Conte-Russian (1980); Bray (1980); Cresswell (1980); Kitson and Guy (1980); Nicholls (1981); R. Young (1981); Crowley (1982); Industrial Risk Insurers (1982); Pignato (1983); Wass (1983); Anon. (1984k); Angelini (1984); Watson (1984); Billinge, Moodie and Beckett (1986); Hodnett (1986a–c); Mullhaupt (1986); API (1987 Publ. 2030); Theobald (1987a,b); Murrell (1988); Theobald, Westley and Whitbread (1988); Thorne, Theobald and Melinek (1988); W.S. Wood (1988); Yao (1988); Lev and Strachan (1989a,b); McCaffrey (1989); Vasey (1989); Chow and Fong (1991); FMRC (1991); Lev (1991); Melinek (1993b); Jackman and Nolan (1994)

Steam systems
Steam curtains: Cairney and Cude (1971); Simpson (1971)
Steam snuffing: Runes and Kaminsky (1965, 1973); Müller-Dethlefs and Schlader (1976)

Fire extinguishing agents and systems
Guise and Zeratsky (1965, 1982); FMEC (1967); Charney (1969); Hearfield (1970); J.R. Hughes (1970); NFPA (1970/6); Harpur (1971); Haessler (1973); Anon. (1974d); J.L. Bryan (1974); Anon. (1978 LPB 22, p.107); Rushbrook (1979); Riley (1983); Fuchs (1984); HSE (1984 GS 16); Webster (1984); Welker, Martinsen and Johnson (1986); Sharma, Lal and Singh (1987); Ewing *et al.* (1989a); Scheinson, Penner-Hahn and Indritz (1989); Simmonds (1993)
BS 5306: 1976–
Water: Ashill (1966b); G. Clarke (1978); Corlett and Williams (1979); Heskestad (1980); Fritz and Jack (1983); Hodnett (1986a)
Foam: Burgoyne (1949a); Burgoyne, Katan and Richardson (1949a); Bikerman *et al.* (1953); Perri (1953); Bartkowiak, Lambiris and Zabetakis (1959); Hird and Fippes (1960); Burgoyne and Steel (1962); Underwriters Laboratories (1963); Jensen (1964); Vervalin (1964b,d); Meldrum and Williams (1965); Ashill (1966); G. Nash (1966); Hearfield (1970); Hird, Rodrigues and Smith (1970); J.R. Hughes (1970); J.R. Williams (1970); FRS (1972 Fire Res. Note 925, 1973 Fire Res. Note 980, 993, 1974 Fire Res. Note 1007); Meldrum (1972, 1982); Sylvia (1972e); P. Nash (1973b, 1984); Corrie (1974, 1977); E.M. Evans and Whittle (1974); Anon. (1975c); BRE (1975 CP 25/75, CP 42/75, 1976 CP 74/76, 1978 CP15/78); Anon. (1976b); Burford (1976); Elliott and Chiesa (1976); MITI (1976); Gillespie and Dimaio (1977); Klunick (1977); P. Nash and Whittle (1978); Woodman *et al.* (1978); L.E. Brown and Romine (1979, 1981); Chiesa (1980); Lev (1981b); Murphy (1981); Anon. (1983k); Boughen (1983); Dimaio and Lange (1984); Dimaio, Lange and Cone (1984); J.L. Evans (1985, 1988); SKUM (1986); Lockwood (1986); Briggs and Webb (1988); NFPA (1988 NFPA 11, 11A, 16A, 1990 NFPA 11C, 1991 NFPA 16); Tabar (1989); Harker (1990); Waters (1990 LPB 91); M. Clarke (1992); Anon. (1993d); Howells (1993, 1993 LPB 114)
BS 5306: Pt 6: 1988–
Inert gas, including carbon dioxide: McGuire (1964); Atallah and Wohl (1965); Williamson (1986); Bryant (1991); NFPA (1993 NFPA 12)
Solid carbon dioxide: Burgoyne, Katan and Richardson (1949b)
Dry chemicals: Fire Control Engineering Co. (n.d.); Dolan (1957); McCamy, Shoub and Lee (1957); Lafitte and Bouchet (1959); T.G. Lee and Robertson (1960); Underwriters Laboratories (1963); Dewitte, Vrebosch and van Tiggelen (1964); Tuve (1964); Vervalin (1964e); Laffitte *et al.* (1965); Meldrum and Williams (1965); Anon. (1966b); W.E. Wilson, O'Donovan and Fristrom (1969); Birchall (1970); Dodding, Simmons and Stephens (1970); Emmrich (1971); Wesson (1972); Woolhouse and Sayers (1973); Schweinfurth (1974); Anon. (1975b); Iya, Wollowitz and Kaskan (1975); McHale (1975); Spence and McHale (1975); Stauffer (1975); MITI (1976); Morikawa (1976); Dixon-Lewis and Simpson (1977); Russell (1977); Vanpee and Shirodkar (1979); Mitani (1981, 1982, 1983); Boughen (1982); Mitani and Niioka (1982); Haessler (1986); Ewing *et al.* (1989b); NFPA (1990 NFPA 17)
BS 5306: Pt 7: 1988
Particulate materials: Sharma *et al.* (1992)

Vaporizing liquids, halons: Burgoyne and Richardson (1949a); Belles and O'Neal (1957); Garner *et al.* (1957); Rasbash (1968); Homann and Poss (1972); Sylvia (1972d); Tatem, Gann and Carhart (1973a,b); Anon. (1974–); Hirst (1974a,b); NFPA (1975/13, 1990 NFPA 12B, 1992 NFPA 12A); Gann (1976); Williamson (1976); FRS (1977 Fire Res. Note 1073); Gann *et al.* (1978); P.F. Thorne (1978b,c); Wiersma (1978); Boughen (1979); Peterson (1979); Anon. (1981t); Tucker, Drysdale and Rasbash (1981); Peissard (1982); Westbrook (1982c); Capper (1983); Mitani (1983); C.C. Grant (1985); D.W. Moore (1986)
BS 5306: Pt 5: 1982–
Alternatives to halons, clean agents: Molina and Rowland (1974); Anon. (1991g); G. Taylor (1991); Senecal (1992a,b); B. Ward (1992); Hough (1993); McKay (1993); NFPA (1994 NFPA 2001)
Gels: Ishida and Iwami (1984)
Combustible metal agents: McCormick and Schmitt (1974); Prokopovitsh (1986)
Fixed equipment: Anon. (1974–); Schweinfurth (1974); Anon. (1975b,c); Stauffer (1975); Burford (1976); Rasbash (1976a); P. Nash (1977b); Boughen (1982, 1983); J.L. Evans (1985); FPA (1990 PE 6)
Halon systems: Williamson (1976); Wiersma (1978); Boughen (1979); Anon. (1981t); Forrester (1982); Peissard (1982); C.C. Grant (1985); Hoskins (1985); R.J. Martin, Shepherd and Hamlin (1986); Goodall (1988); Genge (1989); Sreeves (1989); Whiteley (1989); Boyce (1990)
Mobile and portable equipment: Fire Offices Committee (n.d.a); Guccione (1961); Lockwood (1965, 1973b); BRE (1975 CP 82/75); P. Nash (1969, 1975a, 1991); R. Russell (1977); M.E. Petersen (1986a,b); FPA (1988 CFSD PE 3, 1990 CFSD PE 4); NFPA (1990 NFPA 10)
BS 5423: 1987
Fire points: FPA (1974 S6, 1988 CFSD PE 2)

Fire protection of particular activities, equipment
Air compressors: Duguid (1965)
Bin storage: Field and Murrell (1988)
Cables: IRI (1965/6); F.E. Baker and Shepherd (1971); Kirkham (1987); Annemaier and Graf (1988); Woolhead (1989, 1990)
Computers: IRI (1971/8); Bray (1973); Pucill (1973); Mottershead (1977); NFPA (1992 NFC 75)
Control systems: Castle (1984)
Crushing and grinding equipment: FPA (CFSD FS 6033)
Dip tanks, heat treatment baths: HSE (1971 HSW Bklt 27); Orey (1972b); FPA (1974 S8)
Documentation, records: FPA (1974 S7); NFPA (1991 NFPA 232)
Drum stores: Delichatsios (1982); Miklouicich and Noronha (1982); Rogerson (1982); Capizzani (1985)
Electrical equipment: FPA (1968/6, 1974/25, 1990 CFSD FS 6014); NFPA (1990 NFPA 70B, 1991 NFPA 79, 1993 NFPA 70)
Gas and vacuum systems: NFPA (1993 NFPA 99C)
Heat transfer systems: Fuhr (1992)
Hydraulic oil systems: FPA (1976 CFSD FS 6016)
Incinerators : FPA (S3, 1987 CFSD GP 9)
Oil burners: FPA (1989 CFSD FS 6042)
Pilot plants: Capraro and Strickland (1989)
Pneumatic conveying: NFPA (1990 NFPA 650)
Power stations: NFPA 1992 NFPA 850)
Reciprocating compressors: FPA (CFSD FS 6034)
Valves: Arant (1981); Choquette (1984); Symalla (1984); Varey (1988)
Turbines: NFPA (1990 NFPA 37)
Vaporizers: Bowman and Perkins (1990)
Vessels and tanks: Pettit (1945); Hird, Rodrigues and Smith (1970); Kletz (1971, 1974e, 1975d, 1977d,k, 1986g); Bray (1964, 1966); Thomas and Law (1965 FRS Fire Res. Note 609); Anon. (1966d); Chaillot (1966); FPA (1966); Warren (1966); Hearfield (1970); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); Vervalin (1973f); van Eijndhoven, Nieuwenhuizen and Wally (1974); Nash and Young (1975 BRE CP 42/75); Kaefer (1977); Peyton (1984); Smith (1984); I. Williams (1984); B.M. Lee (1989); Droste (1992); Meiers and Jarman (1993); M. Wilson (1993)
Construction activities: NFPA (1989 NFPA 241)
Transport: NFPA (Appendix 27, 1973/10); Fitch (1986); Keller, Kerlin and Loeser (1986); McGinley (1986)
Jetties: Dicker and Ramsey (1983)
Waste disposal activities: FPA (1971/15)

Oxygen enriched atmospheres
HSE (1984 HSE 8); NFPA (1990 NFPA 53M)

Fire security, arson prevention
FPA (CFSD AR, MR, SEC series, 1972/16, 19, 1989 CFSD OR 7); NFPA (1986 NFPA 602, 1992 NFPA 601)

Fire fighting
FPA (CFDS FPDG 5); Rasbash and Stark (1960); Risinger (1964b,c,e–g); Zeratsky (1964); O'Dogherty (1965); NFPA (1966–/4, 1972/8, 1974/11, 1975/16, 1985/18); Guise (1967, 1975, 1976); Methner (1968); Home Office (1972/9, 1974– *Manual of Firemanship*, 1974/10); HSE (1970 HSW Bklt 10); J.R. Hughes (1970); Rawill (1971); Stark (1972, 1976); Sylvia (1972b); W.E. Clark (1974); PITB (1975/6); Clayton (1976); Hodnick (1976); Lawson and Rasbash (1976); Brennan and Stow (1977); Austin (1979); Ishida and Iwama (1984); P.F. Johnson (1986); Klem and Saunders (1986); Purington (1986); Rosenhah (1986); P.O. Davis and Dotson (1987); Nazario (1988); E. Meyer (1989); Gore, Evans and McCaffrey (1991); A. Evans (1994)
BS (Appendix 27 *Fire Protection, Hoses and Hose Couplings*), BS 5041: 1974–; BS 5274: 1985; BS 3165: 1986; BS 3169: 1986; BS 336: 1989
Liquid fires: Rasbash and Rogowski (1957); Rasbash (1960); Rasbash and Stark (1960, 1962); Sylvia (1972b,e); P. Nash (1973b, 1974b); Corrie (1974); Capper (1985)
Dilution of water-soluble liquids: Thorne (1978a)
LNG fires: Petersen, Morizumi and Carpenter (1968); Welker, Wesson and Sliepcevich (1969); Welker and Sliepcevich (1970); Walls (1971, 1973); Wesson, Welker and Brown (1972, 1975); Wesson *et al.* (1973a,b); Welker, Wesson and Brown (1974); Guise (1975, 1976); H.H. West, Brown and Welker (1975); Bellus, Vincent *et al.* (1977); Wesson and Associates (1977); L.E. Brown and Romine (1979, 1981); Boughen (1980); Lev (1981a, b); Lee (1989)

LPG fires: Martinsen (1982); Williams (1984); Blomquist (1988); B.M. Lee (1989)
Tank fires: Risinger (1964b,f,g); J.R. Hughes (1970); Stillman (1971); E.M. Evans and Whittle (1974); Herzog (1974, 1979); Mahley (1975); NFPA (1975/16); P. Nash and Whittle (1978); Kletz (1982 LPB 47); B.M. Lee (1989); API (1991 Publ. 2021)
Metal, metal powder fires: Reuillon *et al.* (1977); NFPA (1987 NFPA 51); Sharma, Lal and Singh (1987); Varshney, Kumar and Sharma (1990); Cardillo and Nebuloni (1992); Sharma, Varshney and Kumar (1993)
Sulphur fires: NFPA (1988 NFPA 655)
Wood fires: Tamanini (1976)
Transport fires: W. Ward (1978); Home Office (1985 *Manual of Firemanship* Bk 4)
Water curtains: Rielsch (1979); Stephenson and Coward (1987); Maini and Stephenson (1989); Coppalle, Nedel and Bauer (1993)
Thermal image aids: Blatte (1985); Treliving (1985)
Fire fighting hazards: OSHA (n.d./1); Lathrop (1977)
Gas cylinders: CGA (1990 SB-4)
Breathing apparatus: NFPA (1989 NFPA 1404)
Protective clothing: Abbott and Schulman (1976); Holcombe (1981); Anon. (1982/83); NFPA (1990 NFPA 1991–1993)
BS (Appendix 27 *Personal Protection*), BS 1547: 1969; BS 3791: 1970; BS 4667: 1974–
Radiation control: NFPA (1960/2)
Smokehoods: B. Brown (1989)

Fire services (*see also* Table 24.1)
Home Office (1974– *Manual of Firemanship*); FPA (1988 CFSD OR 2, 1990 CFSD OR 1)
Fire communications: NFPA (1972/8)
Occupational fire services: FPA (CFSD MR 11, 1989 CFSD MR 14)

Human behaviour in fires
Wood (1972 FRS Fire Res. Note 953); J.L. Bryan (1976, 1978); Carmack (1976); Canter (1980, 1980/81); Jin (1981); Ikeda (1982); Keating (1982); Tong (1983); Wardlaw (1983); Paulsen (1984); BRE (1985 BR 61, IP20/85); E.G. Butcher (1985); Ramachandran (1990a)

Fire response, evacuation
J.M. Watts (1987); FPA (1990 CFSD MR 7); NFPA (1990 NFPA 902M, 1561, 1992 NFPA 471–473)

Fire training
FPA (CFSD M 10, 1974/23, 1987 CFSD M 12, 1989 CFSD M 9); API (1966); B. Martin (1966); NFPA (1968/5, 1988 NFPA 1410); Anon. (1973b); Bruce and Diggle (1974); Long (1975); PITB (1975/6); Vervalin (1975d,e); N. Anderson (1991)

Fire inspection, checklists
Landy (1964a–c); FPA (1965/3); API (1971 Refinery Inspection Guide Ch. 20); NFPA (1994/41)

16.1 Fire

16.1.1 The combustion process

Fire, or combustion, is a chemical reaction in which a substance combines with oxygen and heat is released. Usually fire occurs when a source of heat comes into contact with a combustible material. If a combustible liquid or solid is heated it evolves vapour, and if the concentration of vapour is high enough it forms a flammable mixture with the oxygen of the air. If this flammable mixture is then heated further to its ignition point, combustion starts. Similarly, a combustible gas or vapour mixture burns if it is heated to a sufficiently high temperature.

Thus there are three conditions essential for a fire: (1) fuel, (2) oxygen, and (3) heat. These three conditions are often represented as the fire triangle shown in Figure 16.1. If one of the conditions is missing, fire does not occur and if one of them is removed, fire is extinguished.

Normally the heat required is initially supplied by an external source and then provided by the combustion process itself. The amount of heat needed to cause ignition depends on the form of the substance. A gas or vapour may be ignited by a spark or small flame, while a solid may require a more intense heat source.

Ignition of a combustible gas or vapour mixture may occur in two ways. In the first the energy for ignition is supplied by a local source such as a spark or small flame at a point within the mixture, as shown in Figure 16.2(a). In the second the bulk gas mixture is heated up to its ignition temperature, as shown in Figure 16.2(b).

The three conditions of the fire triangle indicate how fires may be fought. The first method is to cut off the fuel. This is particularly relevant for fires caused by leaks on process plant. The second method is to remove heat. This is usually done by putting water on the fire. The third method is to stop the supply of oxygen. This may be effected in various ways, including the use of foam or inert gas.

Fire is sustained only if there is a net release of heat. The heat comes from the combustion of fuel. If this fuel is liquid or solid, it must first be vaporized. With liquids or solids fire usually involves a process of positive feedback. The heat evolved by the fire causes the vaporization of an increasing amount of fuel and the fire spreads.

Development of the fire depends on the situation of the fuel. This is commonly illustrated by considering the

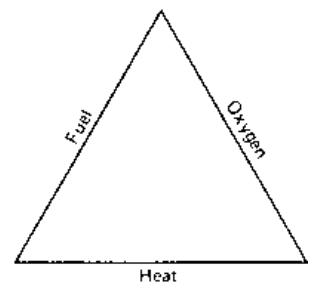


Figure 16.1 *The fire triangle*

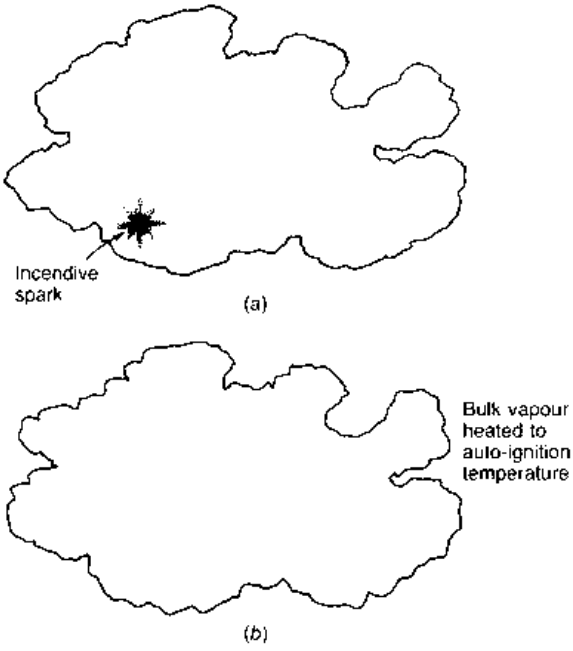


Figure 16.2 *Ignition of a flammable mixture: (a) local ignition and (b) bulk gas ignition*

difference in modes of burning of a lighted match held upwards or downwards. Thus the stacking of material in closely spaced vertical piles in a warehouse may tend to encourage fire spread.

Fire needs to be supported by the ignition source until it is self-sustaining. For this, duration may be more important than temperature. Thermite bombs, which reach about 1650°C for 15–20 s, have been found less effective in starting fires than napalm, which reaches about 1100°C for 10–15 min.

Different parts of a fire have different heat balances. In some parts, particularly near the edge of the fire, the heat balance may be only just positive. It is sometimes good sense, therefore, to direct fire extinguishant to those parts of the fire and so hit it at its weakest points.

It is not necessarily essential to remove all the oxygen in order to extinguish a fire. Liquid fires can generally be put out by reducing the oxygen concentration below 12–16%. Solids fires may require a greater reduction of oxygen concentration – below about 5% for surface smouldering and as low as about 2% for deep-seated smouldering.

16.1.2 Fire growth and spread

Fire normally grows and spreads by direct burning, which results from impingement of the flame on combustible materials, by heat transfer or by travel of the burning material.

The three main modes of heat transfer are (1) conduction, (2) convection and (3) radiation. All these modes are significant in heat transfer from fires. Conduction is important particularly in allowing heat to pass through a solid barrier and ignite material on the other side.

Most of the heat transfer from fires, however, is by convection and radiation. It is estimated that in most fires some 75% of the heat emanates by convection. The hot products of combustion rising from a fire typically have a temperature in the range 800–1200°C and a density a quarter that of air. On open plant much of the heat is dissipated into the atmosphere, but in buildings it is transferred to the ceiling.

Radiation is the other main mode of heat transfer. Although it usually accounts for a smaller proportion of the heat issuing from the fire, radiated heat is transferred directly to nearby objects, does not go preferentially upwards and crosses open spaces. For these reasons it is generally the most significant mode of transfer on open plant.

An account of the modes of heat transfer is given in *Heat Transfer in Fire* (Blackshear, 1974). Radiant heat transfer is treated in *Thermal Radiation Heat Transfer* (Siegel and Howell, 1991).

The other way in which fire spreads is by travel of bulk materials, such as burning liquids or solid brands. With fires in buildings particularly, a stage is generally reached when the materials have been heated up to the point where they give off flammable vapours. The rapid spread of fire which occurs at this point is called 'flashover'.

16.1.3 Classification of fires

There are several classification systems for fires. In the UK, the BS classification is given in BS EN2: 1992 *Classification of Fires*. This classification is:

Class A Fires involving solid materials, usually of an organic nature, in which combustion takes place with the formation of glowing embers.
Class B Fires involving liquids or liquefiable solids.
Class C Fires involving gases.
Class D Fires involving metals.

BS EN2: 1992 replaces BS 4547: 1972.

In the USA, the NFPA classification is given in the NFPA Codes. NFPA 10: 1984 contains the following classification:

Class A Fires in ordinary combustible materials, such as wood, cloth, paper, rubber and many plastics
Class B Fires in flammable liquids, oils, greases, tars, oil base paints, lacquers, and flammable gases.
Class C Fires which involve energized electrical equipment where the electrical conductivity of the extinguishing media is of importance.
Class D Fires in combustible metals, such as magnesium, titanium, zirconium, sodium, lithium, and potassium.

This classification has obvious relevance to the extinguishing medium to be used. For a Class C fire, when electrical equipment is de-energized, extinguishers for Class A and B fires may be used.

Fires are also classified by size. The classification recommended by the Central Fire Brigades Advisory

Council and given in the *Manual of Firemanship* by the Home Office (1974–) is:

Major fire	$\geq$ 20 jets
Large fire	8–19 jets
Medium fire	3–7 jets
Small fire	1–2 jets, or $\geq$ 3 hose reels
Minor fire	1–2 hose reels, or hand extinguishers

The classifications of combustible and flammable liquids given in Chapter 10 are also relevant.

16.1.4 Classification of fires: process industries

With regard to fires in the process industries specifically, fires may be classified broadly into the following categories:

(1) vapour cloud fires –
  (a) fires with no explosion,
  (b) fires resulting from explosion,
  (c) fires resulting in explosion;
(2) fireballs;
(3) jet flames;
(4) liquid fires –
  (a) pool fires,
  (b) running liquid fires;
(5) solids fires –
  (a) fires of solid materials,
  (b) dust fires;
(6) warehouse fires;
(7) fires associated with oxygen.

Many major fires are vapour cloud fires. It is convenient to term the three categories of vapour cloud fire, or flash fire, as

Type 1	Fires with no explosion.
Type 2	Fires resulting from explosions.
Type 3	Fires resulting in explosions.

16.2 Flammability of Gases and Vapours

Combustion of a flammable gas–air mixture occurs if the composition of the mixture lies in the flammable range and if the conditions exist for ignition. As already mentioned, ignition may result from either (1) bulk gas temperature rise or (2) local ignition.

The combustion of the mixture occurs if the bulk gas is heated up to its auto-ignition temperature. Alternatively, combustion occurs if there is applied to the mixture a source of ignition which has sufficient energy to ignite it.

Accounts of flammability characteristics and collections of flammability data are given in *Limits of Flammability of Gases and Vapours* (Coward and Jones, 1952 BM Bull. 503) and *Flammability Characteristics of Combustible Gases and Vapours* (Zabetakis, 1965 BM Bull. 627). A further description of flammability characteristics is given by Burgoyne (1965a). Flammability data are also given in the *Handbook of Industrial Loss Prevention* (FMEC, 1967) and the ICI *Electrical Installations in Flammable Atmospheres Code* (ICI/RoSPA, 1972 IS/91).

The discussion of flammability characteristics given below assumes, unless otherwise stated, that the flammable gas mixture is with air and that the pressure and temperature conditions are the initial values. Selected references on flammability and ignition characteristics are given in Table 16.3.

Table 16.3 Selected references on flammability and ignition characteristics

SMRE (Fire 3); Factory Mutual Insurance Co. (1940); NFPA (1972/9, 1990 NFPA 30, 704, 1991 NFPA 49, 325M, 491M, 1991/27); FPA (1974/22); Cruice (1986); Gerlach (1987); Bond (1991)
BS (Appendix 27 *Test Methods*)

Flammability
Affens (1968); Affens, Carhart and McLaren (1977); Bajpai (1980)

Flammability limits
Mallard and Le Chatelier (1883); Le Chatelier (1891); Le Chatelier and Boudouard (1898); Burgess and Wheeler (1911); Coward and Brinsley (1914); A.G. White (1922, 1924); G.W. Jones (1928, 1937, 1938); Goldmann (1929); G.W. Jones *et al.* (1935 BM RI 3278); Hsieh and Townend (1939b); Zeldovich (1941); Drozdov and Zeldovich (1943); G.W. Jones *et al.* (1945 BM RI 3826); Burgoyne (1948, 1949a); Egerton and Powling (1948); Matson and Dufour (1950); Underwriters Laboratories (1950); Fenn (1951); B. Lewis and von Elbe (1951, 1961, 1987); Zabetakis, Scott and Jones (1951); Coward and Jones (1952 BM Bull. 503); Egerton and Thabet (1952); Spakowski (1952); Burgoyne and Neale (1953a,b); Egerton (1953); Simon, Belles and Spakowski (1953); Zabetakis and Jones (1953); Zabetakis and Richmond (1953); Burgoyne and Hirsch (1954); Umland (1954); J.A. Browning and Krall (1955); Wolfson and Dunn (1956); Delbourgo and Laffitte (1957); Linnett and Simpson (1957); Meyer (1957); Spalding (1957d); Dalmai (1958); Dixon-Lewis and Isles (1959, 1961); Zabetakis, Lambiris and Scott (1959); Bartkowiak and Zabetakis (1960 BM RI 5610); Berlad (1961); Kuchta *et al.* (1961 BM RI 5877); Monger, Sello and Lehwalder (1961); K.N. Palmer and Tonkin (1961); Buckley and Husa (1962); Kuchta, Lambiris and Zabetakis (1962 BM RI 5992); Pusch and Wagner (1962); van Tiggelen and Burger (1964); G.S. Scott (1965 BM RI 6659); Zabetakis (1965 *BM Bull.* 627); Craven and Foster (1966); FMEC (1967); D.J. Miller and Webb (1967); Prugh (1967); Yang and Gray (1967); Kuchta *et al.* (1968); Burgess (1969); W.B. Howard (1970a); Rozlovsky (1970); Furno *et al.* (1971); Lovachev (1971, 1979); Lu, Dabora and Nicholls (1971); Steen (1971, 1974); Grove, Patel and Webster (1972); Homann and Poss (1972); Andrews and Bradley (1973b); Gerstein and Stine (1973); Halstead, Prothero and Quinn (1973); Lovachev *et al.* (1973); Tien (1973); Halstead, Pye and Quinn (1974); Burgess and Hertzberg (1975); Sorenson, Savage and Strehlow (1975); Hertzberg (1976 BM RI 8127); Meadows (1976); Crescitelli *et al.* (1977); G.F.P. Harris and MacDermott (1977); Hilado and Cumming (1977, 1979); Viallon (1977); FPA (1978 Fire Res. Note 1078); Jarosinski and Strehlow (1978); Nettleton (1978a, 1979, 1980b); D.C. Bull (1979); Macek (1979); Yamaoka and Tsuji (1979); Ale, Bruning and Koenders (1980); Mitani (1980); P. Roberts, Smith and Ward (1980); Buckmaster and Mikolaitis (1982); Crescitelli *et al.* (1982); Hertzberg (1982, 1985); Zalosh (1982); Kanury (1983); von Lavante and Strehlow (1983); Palazzi *et al.* (1984); ASTM (1985 E681); Peters and Smooke (1985); M.S. High (1987); Hustad and Sonju (1988); Kletz (1988a); Tam and Ludford (1988); Wierzba, Karim and

Cheng (1988); Wierzba, Harris and Karim (1990); Ishizuka (1991); Lakshimisha, Paul and Mukunda (1991); Law and Egolfopoulos (1991, 1992); Seaton (1991); Conrad *et al.* (1992); Hansel, Mitchell and Klotz (1992); Gibbon, Wainwright and Rogers (1994)
Effect of diluents: Burgoyne and Williams-Leir (1948a,b); Egerton (1953); Mellish and Linnett (1953); Atalla and Wohl (1965); Zabetakis (1965 BM Bull. 627); Hirst and Booth (1977); Crescitelli, Russo and Tufano (1979b); Mitani (1981); Hirst and Savage (1981/82); P. Roberts and Smith (1983); Plett (1984); Lihou (1993)
Oxygen concentration: Denison *et al.* (1968); Huggett (1973); Nguyen and Branch (1987); Subramanian and Cangelosi (1989)
Oxygen-enriched atmospheres: ASTM (1983 STP 812); HSE (1984 HSE 8); NFPA (1990 NFPA 53M)

Flammability of mists
Burgoyne (1949b, 1963); Burgoyne and Cohen (1954); J.A. Browning and Krall (1955); Hayashi *et al.* (1981)

Flammability of liquids
Burgoyone and Williams-Leir (1949); Anon. (1973c); Steen (1974)

Flashpoint, fire point
FRS (Fire Res. Note 1022); BDH (1962); Johnston (1974); Lenoir (1975); Li and Moore (1977); Lance, Barnard and Hooyman (1979); Loader (1981); Kanury (1983); ASTM (1984 E502, 1990 D92, D93); Riazi and Daubert (1987); Nakano, Hirai and Hayashi (1990); Bothe and Brandes (1992)
BS 6664: 1986–; BS 2000: Pt 35: 1993
Vapour pressure: T.E. Jordan (1954)

Autoignition temperature, spontaneous ignition temperature
Townend and Madelkar (1933); Le Chatelier (1937); Silver (1937); Matson and Dufour (1950); Underwriters Laboratories (1950); J.L. Jackson (1951); Coward and Jones (1952 BM Bull. 503); Setchkin (1954); Zabetakis, Furno and Jones (1954); Riddlestone (1958); Vanpee and Wolfhard (1959); Affens, Johnson and Carhart (1961); Zabetakis, Scott and Kennedy (1962 BM RI 6112); Kuchta, Cato and Zabetakis (1964); Kuchta, Bartkowiak and Zabetakis (1965 BM RI 6654); J.A. MacDonald and White (1965); Ashmore and Preston (1967); FMEC (1967); B.F. Gray (1970); Hilado and Clark (1972a,b); Affens and Carhart (1974); Beerbouwer (1974); Santon (1976); Halstead, Kirsch and Quinn (1977); Stull (1977); D.J. Lewis (1980a); Cudahy and Troxler (1983); FPA (1984 CFSD NB 5); C. Robinson and Smith (1984); Ashmore and Blumson (1987 LPB 75); Snee (1988 LPB 81); Conti and Hertzberg (1989); Oberhagemann and Schecker (1989); S.M. Richardson, Saville and Griffiths (1990); J.F. Griffiths *et al.* (1991); Egolf and Jurs (1992); J.F. Griffiths *et al.* (1992); Lakshimisha *et al.* (1992); J.F. Griffiths (1993); J.F. Griffiths, Halford-Maw and Rose (1993)

Liquid ignition temperature
N.J. Thompson (1929); Setchkin (1954); Malychuk and Gollahalli (1987)

Ignition energy
Blanc *et al.* (1947, 1949); Fenn (1951); Swett (1955, 1956, 1957); Brokaw and Gerstein (1957); Riddlestone (1957); Litchfield (1960 BM RI 5671); Ashman and Büchler (1961); Rae, Singh and Danson (1964); Slack and Woodhead (1966); FMEC (1967); Bartels and Howes (1971); de Soete (1971); Moorhouse, Williams and Maddison (1974); Ballal and Lefebvre (1975b); Bartels (1975a); Rao and Lefebvre (1976); Halm (1979); CMI (1980 CMI 803301–1); H. Kramer (1987); Sloane and Schoene (1989); Frendi and Sibulkin (1990); Glor and Siwek (1992); Chin-Shu Wang and Sibulkin (1993)

Burning velocity
Gouy (1879); Payman and Wheeler (1922); Fiock and Marvin (1937a,b); Zeldovitch and Frank-Kamenetsky (1938); Fiock *et al.* (1940); Tanford (1947); Tanford and Pease (1947); Culshaw and Garside (1949); M.E. Harris *et al.* (1949); Linnett and Hoare (1949, 1951); Strickland-Constable (1949); Gerstein, Levine and Wong (1950); Coward and Jones (1952 BM Bull. 503); Dugger and Simon (1953); Linnett (1953); Manton, von Elbe and Lewis (1953); Egerton and Lefebvre (1954); J.A. Browning and Krall (1955); Bundy and Strong (1955); Fiock (1955); D.G. Martin (1956); Spalding (1956, 1957a–c); Brokaw and Gerstein (1957); Gilbert (1957); Golovina and Fyodorov (1957); D. Smith and Agnew (1957); Eschenbach and Agnew (1958); Gibbs and Calcote (1959); O'Donovan and Rallis (1959); Schotte and Vaags (1959a,b); Spalding and Yumlu (1959); Strauss and Edse (1959); Agnew and Graiff (1961); Raezer (1961); Yang (1961); Dugger (1962); Kuehl (1962); Raezer and Olsen (1962); Rallis, Garforth and Steinz (1965); Andrews and Gray (1964); Armitage and Gray (1965); Lefebvre and Reid (1966); Yumlu (1967a,b, 1968); Fells and Rutherford (1969); Palm-Leis and Strehlow (1969); Edmondson and Heap (1970, 1971); D. Bradley and Hundy (1971); S.B. Reed (1971); Spalding, Stephenson and Taylor (1971); Andrews and Bradley (1972a,b, 1973a); Peschel and Fetting (1972); Simmons and Wright (1972); Halstead, Prothero and Quinn (1973); P.L. Stephenson and Taylor (1973); Halstead, Pye and Quinn (1974); Nair and Gupta (1974); Putnam (1974); Müller-Dethlefs and Schlader (1976); Garforth and Rallis (1978); Sriramulu, Padiyar and Shet (1978); Putnam, Ball and Levy (1980); Agrawal (1981); Dixon-Lewis and Islam (1982); Gülder (1982); Liu and MacFarlane (1983); Tufano, Crescitelli and Russo (1983); Ronney and Wachman (1985); Yamaoka and Tsuji (1985); Iijima and Takeno (1986); Yu, Law and Wu (1986); P.G. Hill and Hung (1988); Göttgens, Mauss and Peters (1992); Sher and Ozdor (1992); Koroll, Kumar and Bowles (1993)
Turbulent burning velocity: Damköhler (1940); Shchelkin (1943); Bollinger and Williams (1949); D.T. Williams and Bollinger (1949); Karlovitz, Denniston and Wells (1951); Wohl *et al.* (1953); Wohl (1955); Wohl and Shore (1955); J.M. Richardson (1956); Richmond, Singer *et al.* (1957); Fine (1958); Shetinkov (1959); Kozachenko (1962); Lefebvre and Reid (1966); Vinckier and van Tiggelen (1968); Palm-Leis and Strehlow (1969); Sanematsu (1969a,b); Annand (1970); Bhaduri (1970); Mizutani (1972); Andrews, Bradley and Lwakabamba (1975a,b); Abdel-Gayed and Bradley (1977, 1982); Gokalp (1980); Abdel-Gayed, Bradley and Lawes (1987); Sivashinsky (1988); Liu and Lenze (1989); Catlin and

Linstedt (1991); D. Bradley, Lau and Lawes (1992); D. Bradley, Gaskell and Gu (1994)

Quenching
Blanc *et al.* (1947); R. Friedman (1949); M.E. Harris *et al.* (1949); Wohl (1953); Loison, Chaineaux and Delclaux (1954); Berlad and Potter (1955); Brokaw and Gerstein (1957); Potter and Berlad (1957); Singer and von Elbe (1957); Anagnostou and Potter (1959); Wolfhard and Bruszak (1959 BM RI 5457, 1960); Potter (1960); Pusch and Wagner (1962); Kydd and Foss (1964); Grove (1966, 1967); Rosser, Inami and Wise (1966); H. Phillips (1971a, b, 1981a); Rozlovski and Zakaznov (1971); E.C. Woodward and Drew (1971); FRS (1973 Fire Res. Notes 973, 990, 1974 Fire Res. Note 1018); Lunn and Phillips (1973); Nair and Gupta (1973); Ryason and Hirsch (1974); Ballal and Lefebvre (1975a, 1977, 1978, 1979); Maekawa (1975); Buckmaster (1976); F.A. Williams (1976b); Jarosinski and Strehlow (1978); Maekawa, Takeichi and Kato (1978); Maekawa and Takeichi (1979); Strehlow, Nichols *et al.* (1979); P. Roberts, Smith and Ward (1980); Chomiak and Jarosinski (1982); Lunn (1982a,b, 1984a); Jarosinski (1983); Dickie and Lunn (1984); Mendoza, Smolensky and Straitz (1993)

Calorific value
FMEC (1967); Association Nationale pour la Protection contre l'Incendie (1972)

Flame temperature
Loomis and Perrott (1928); G.W. Jones, Lewis and Seaman (1931, 1932); G.W. Jones *et al.* (1931); Ministry of Power (1944); Fehling and Leser (1949); Winternitz (1949); Huff, Gordon and Morrell (1951); B. Lewis and von Elbe (1951, 1961, 1987); Thring (1952); Gaydon and Wolfhard (1953); Bundy and Strong (1955); General Electric Co. (1955); Kaskan (1957); Zabetakis, Lambiris and Scott (1959); Berenblut and Downes (1960); Gay *et al.* (1961); Zeleznik and Gordon (1968); Gordon and McBride (1971, 1976); Stull and Prophet (1971); Svehla and McBride (1973); Eisenberg, Lynch and Breeding (1975); J.G. Marshall and Rutledge (1982); Vancini (1982); Chang and Rhee (1983); Rhee and Chang (1985)
Gas specific heats: W.D.M. Bryant (1933); Spencer and Justice (1934); Justi and Lüder (1935); Justi (1938); Spencer and Flannagan (1942); Dodge (1944); Spencer (1945); Hougen and Watson (1947); Prothero (1969); Vancini (1982); Barnard and Bradley (1985); Yaws, Ni and Chang (1988)

Mists and sprays
Haber and Wolff (1923); Burgoyne (1963); Mizutani (1972b); Mizutani and Nishimoto (1972); J.T. Bryant (1975); S.J. Cook, Cullis and Good (1977); Hayashi, Kumagai and Sakai (1977); Nettleton (1978a, 1987); Ballal (1983a,b)

Thermodynamic properties (*see also* Table 11.1)
Westenberg (1957); M.K. Martin and Heywood (1977)

16.2.1 Flammability limits

A flammable gas burns in air only over a limited range of composition. Below a certain concentration of the flammable gas, the lower flammability limit, the mixture is too 'lean', while above a certain concentration, the upper flammability limit, it is too 'rich'. The concentrations between these limits constitute the flammable range. The lower and upper flammability limits (LFL and UFL) are also sometimes called, respectively, the lower and upper explosive limits (LEL and UEL). They are distinct from the detonability limits.

In general, the most flammable mixture corresponds approximately, but not exactly, to the stoichiometric mixture for combustion. It is frequently found that the concentrations at the lower and upper flammability limits are roughly one-half and twice that of the stoichiometric mixture, respectively.

Flammability limits are affected by pressure, temperature, direction of flame propagation, gravitational field and surroundings. The limits are determined experimentally and the precise values obtained depend, therefore, on the particular test method.

Although there is no universally used equipment, one which has been utilized for the measurement of many flammability limit data is the Bureau of Mines apparatus, which is described by Coward and Jones (1952 BM Bull. 503) and which consists of a cylindrical tube 5 cm diameter and 1.5 m high. The tube is closed at the top but open at the bottom. Gas–air mixtures of different compositions are placed in the tube and a small ignition source is applied at the bottom. The lower and upper limit concentrations at which the flame initiated by the source of ignition just travels the full length of the tube are then determined.

The test is normally carried out with the mixture at atmospheric pressure and temperature and with upward flame propagation, but other conditions can be investigated such as different pressures and temperatures, downward flame propagation and/or addition of inert gases. Table 16.4 shows flammability limits of selected substances. It also gives other flammability characteristics which are described below.

For many organic substances the lower flammability limit, expressed in mass per unit volume, lies within a relatively narrow range. Burgoyne (1963) quotes data which show the limits as lying mainly in the range 0.04–0.10 g/l (or oz/ft^3). More specifically, he states that for saturated hydrocarbons the lower flammability limit is of the order of 0.045 g/l (oz/ft^3). For unsaturated hydrocarbons it is less and for oxygenated hydrocarbons it is more.

Flammability limits are affected by pressure. Normal variations of atmospheric pressure do not have any appreciable effect on flammability limits. The effect of larger pressure changes is not simple or uniform, but is specific to each mixture. A decrease in pressure below atmospheric can narrow the flammable range by raising the lower flammability limit and reducing the upper flammability limit until the two limits coincide and the mixture becomes non-flammable. This effect is illustrated for methane in Figure 16.3.

Conversely, an increase in pressure above atmospheric can widen the flammable range by reducing the lower flammability limit and raising the upper flammability limit. This effect is shown in Figure 16.4 for natural gas. It may be noted that the effect is more marked on the upper than on the lower flammability limit. In the case of higher hydrocarbons, increase in pressure causes an abnormal increase in the upper flammability limit with the creation of a region of cool flames (Hsieh and Townend, 1939b). Cool flames are considered further

Table 16.4 *Flammability limits, auto-ignition temperatures and flashpoints of selected substances in air at atmospheric pressure*

	Flammability limit (% v/v)		*Auto-ignition temperature* (°C)	*Flashpoint* (°C)	
	Lower	*Upper*		*Closed cup*	*Open cup*
Acetone	2.6	13	465	−18	−9
Acetylene	2.5	100	305	–	–
Ammonia	15	28	651[a]	–	–
Benzene	1.4[a]	8.0[a]	562[a]	−11	–
n-Butane	1.8	8.4	405	−60	–
Carbon disulphide	1.3	50	90	−30	–
Carbon monoxide	12.5	74	–	–	–
Cyclohexane	1.3	7.8	245	−20	–
Ethane	3.0	12.4	515	−135	–
Ethylene	2.7	36	490	−121	–
Ethylene dichloride	6.2[a]	15.9[a]	413[a]	13	18
Ethylene oxide	3[a]	100[a]	429[a]	–	−20
Hydrogen	4.0	75	400	–	–
Methane	5.0	15.0	540	–	–
Propane	2.1	9.5	450	< −104	–
Propylene	2.4	11	460	−108	–
Styrene	1.1[a]	6.1[a]	490[a]	32	38
Toluene	1.3[a]	7.0[a]	536[a]	4	7
Vinyl chloride	4[a]	22[a]	472[a]	–	−78

Sources: Flammability limits: Zabetakis (1965 BM Bull. 627), except as given in footnote. Autoignition temperature: Zabetakis (1965 BM Bull. 627), except as given in footnote. Flash points: Factory Mutual Engineering Corporation (1967).
[a] Factory Mutual Engineering Corporation (1967).

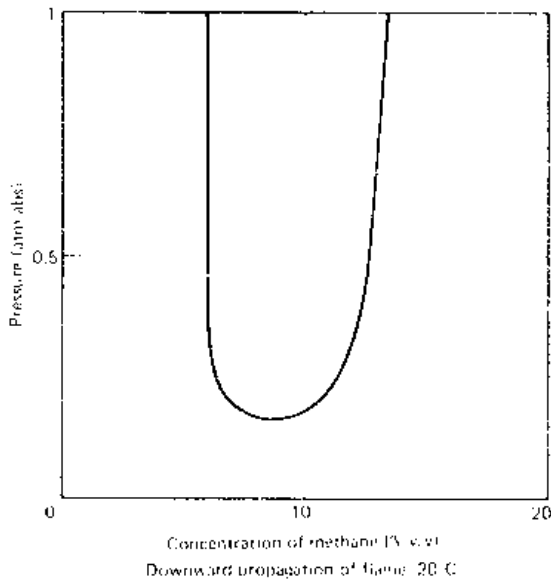


Figure 16.3 *Effect of pressure on flammability limits of methane in air (Coward and Jones, 1952 BM Bull. 503) (Courtesy of the Bureau of Mines)*

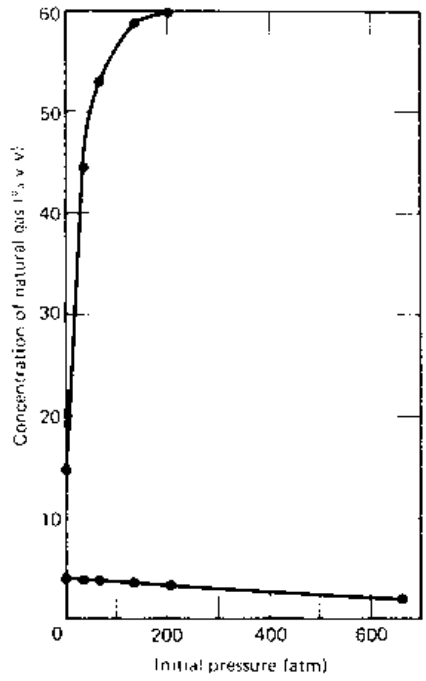


Figure 16.4 *Effect of pressure on flammability limits of natural gas in air (Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

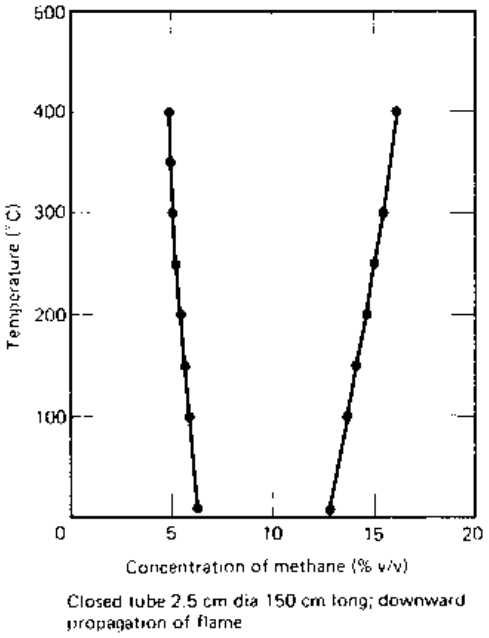


Figure 16.5 *Effect of temperature on flammability limits of methane in air (Coward and Jones, 1952 BM Bull. 503) (Courtesy of the Bureau of Mines)*

below. However, an increase in pressure does not always widen the flammable range; in some cases it can narrow it.

Flammability limits are also affected by temperature. An increase in temperature tends to widen the flammable range. This effect is shown for methane in Figure 16.5. The variation of the lower flammability limit of methane with temperature is illustrated in Figure 16.6. The limit values obtained experimentally fall fairly close to a straight line which passes through the lower limit at 25°C and through zero at the flame temperature of 1225°C.

Similar results are obtained for the effect of temperature on the lower flammability limits of other lower paraffinic hydrocarbons. For these the approximate flame temperature can be taken as 1300°C. Then for the first 10 members of the series from methane to decane

$$\frac{L_t}{L_{25}} = 1 - \frac{t - 25}{1300 - 25} \qquad [16.2.1]$$

where L_t is the lower flammability limit at t°C (%v/v), L_{25} is the lower flammability limit at 25°C (%v/v), and t is the temperature (°C).

The data may also be fairly well correlated by the modified Burgess–Wheeler law, suggested by Zabetakis, Lambiris and Scott (1959):

$$\frac{L_t}{L_{25}} = 1 - \frac{0.75(t - 25)}{\Delta H_c} \qquad [16.2.2]$$

where ΔH_c is the net heat of combustion (kcal/mol).

Likewise the effect of temperature on the upper flammability limits of these hydrocarbons, in the absence of cool flames, may be correlated by the modified Burgess–Wheeler law:

$$\frac{U_t}{U_{25}} = 1 - \frac{0.75(t - 25)}{\Delta H_c} \qquad [16.2.3]$$

where U_t is the upper flammability limit at t°C (%v/v), and U_{25} is the upper flammability limit at 25°C (%v/v).

The variation of flammability limits with temperature was studied by Bodurtha (1980), who obtained for the substances studied a value of 0.0008/°C both for the fractional decrease with temperature of the lower flammability limit and for the fractional increase with temperature of the upper flammability limit.

A more recent study of the effect of pressure and temperature on flammability limits is that of Gibbon, Wainwright and Rogers (1994), who investigated a limited number of solvents. Their work confirmed that an increase in temperature causes a decrease in the lower flammability limit and an increase in the upper flammability limit. They also found that the upper flammability limit increased with increase in pressure. Unexpectedly, the lower flammability limit also increased with increase in pressure.

In sum, the effect of pressure on the flammability limits is much less predictable than that of temperature. In particular, increase in pressure causes in some cases a decrease in the lower flammability limit and in others an increase.

It has been demonstrated that flammability limit measurements can be complicated by surface and vapour phase reactions which occur above the auto-ignition temperature. It has been shown, for example, that methane–air mixtures containing up to 5%v/v methane burn readily at 1000°C. The experiments were conducted with methane concentrations as low as 0.5%v/v (Burgoyne and Hirsch, 1954).

Flammability limits are also affected by the addition of an inert gas such as nitrogen, carbon dioxide or steam. This effect is shown for methane in Figure 16.7. Minimum inert gas contents for suppression of flammability of selected substances in air are shown in

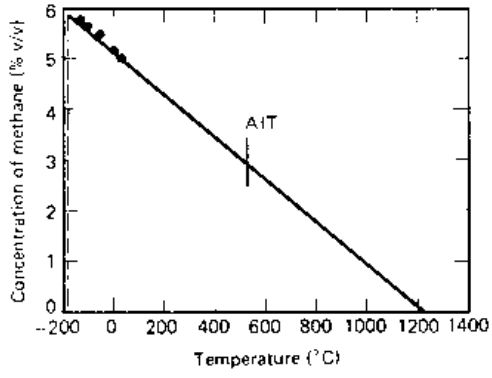


Figure 16.6 *Effect of temperature on low flammability limit of methane in air (Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

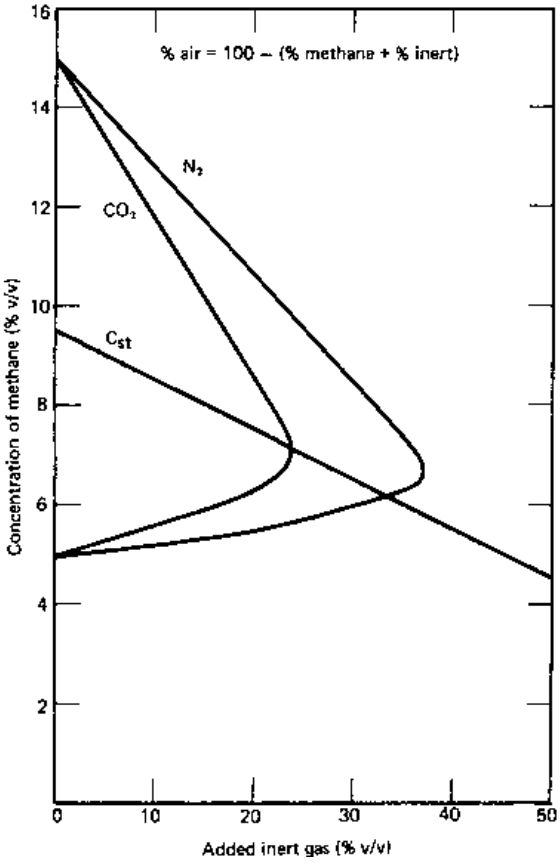


Figure 16.7 *Effect of inert gases on flammability limits of methane in air (Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

Table 16.5. In general, carbon dioxide causes a greater narrowing of the flammable range than does nitrogen. For many flammable gas–air systems, the mixtures can be rendered non-flammable by the addition of about 30% of carbon dioxide or about 40% of nitrogen.

The flammability limits described are those for mixtures of a flammable gas in air. There are also flammability limits for combustion in pure oxygen. In general, the lower flammability limit of a gas is almost the same in oxygen as in air, but the upper flammability limit is much greater in oxygen than in air. The flammable range in oxygen is thus wider than it is in air. The applicability of flammability limits is not confined, however, to air and oxygen. There are flammability limits for substances which burn in chlorine.

Flammability limits for a fuel mixture which contains several flammable gases may be calculated from the equation of Le Chatelier (1891). For the lower limit

$$L = \frac{1}{\sum_{i=0}^{n}(y_i/L_i)} \qquad [16.2.4a]$$

Table 16.5 *Minimum inert gas content for suppression of flammability of selected substances in air (after Burgoyne, 1965a) (Courtesy of the Institution of Marine Engineers)*

	Nitrogen (%v/v)	*Carbon dioxide* (%v/v)
Methane	38	24
Ethane	46	33
Propane	43	30
n-Butane	41	28
n-Pentane	43	29
n-Hexane	42	29
Ethylene	50	41
Propylene	43	30
Benzene	45	32

where L is the lower flammability limit of air-free fuel (%v/v), L_i the lower flammability limit of fuel component i (%v/v) and y_i is the concentration of fuel component i (mole fraction).

For the upper limit

$$U = \frac{1}{\sum_{i=0}^{n}(y_i/U_i)} \qquad [16.2.4b]$$

where U is the upper flammability limit of air-free fuel (%v/v), and U_i the upper flammability limit of fuel component i (%v/v).

Le Chatelier's equation is an empirical one and it is not universally applicable. Its limitations are discussed by Coward and Jones (1952 BM Bull. 503, p. 6). Further information on and examples of the calculation of the flammability limits of fuel mixtures are given in BS 5345: Part 1: 1976.

It is necessary to exercise care in using flammability limit data, since the limit may vary with pressure, temperature and other conditions. The lower flammability limit required to determine the amount of flammable gas–air mixture resulting from a plant leak can probably be obtained quite readily, because usually the data are available for ambient conditions and the accuracy called for is not high, but that required to maintain the concentration of a flammable gas–oxygen mixture entering a reactor just below the flammable range under other pressure and temperature conditions needs greater consideration, because the data may not be available so readily for these other conditions, but they must be accurate.

16.2.2 Ignition temperature

If the temperature of a flammable gas–air mixture is raised in a uniformly heated apparatus it eventually reaches a value at which combustion occurs in the bulk gas. For the range of flammable mixtures there is a mixture composition which has the lowest ignition temperature. This is the minimum spontaneous ignition temperature (SIT) or auto-ignition temperature (AIT).

The auto-ignition temperatures for the first 10 paraffinic hydrocarbons are as follows (Zabetakis, 1965 BM Bull. 627):

	AIT (°C)		*AIT* (°C)
Methane	537	*n*-Hexane	223
Ethane	515	*n*-Heptane	223
Propane	466	*n*-Octane	220
n-Butane	405	*n*-Nonane	206
n-Pentane	258	*n*-Decane	208

It may be noted that there is a break between the auto-ignition temperature for *n*-butane and that for *n*-pentane and that the rate of decrease of these temperatures after *n*-pentane is low. Some substances have quite low auto-ignition temperatures. The auto-ignition temperature of carbon disulphide, for example, is 90°C.

The auto-ignition temperature is a property which is particularly liable to variations caused by the nature of hot surfaces. The values normally quoted are obtained in laboratory apparatus with clean surfaces. The auto-ignition temperature may be reduced by as much as 100–200°C for surfaces which are lagged or are contaminated by dust.

Auto-ignition temperatures of selected substances are given in *Table 16.4*.

16.2.3 Ignition time delay

Ignition of a flammable mixture raised to or above the temperature at which spontaneous ignition occurs is not instantaneous; there is a finite time delay before ignition takes place. This time delay decreases as the ignition temperature increases and the reduction has been correlated by Semenov (1959) using the equation

$$\ln \tau = \frac{k_1 E}{T} + k_2 \qquad [16.2.5]$$

where E is the apparent activation energy, T is the absolute temperature, t is the time delay before ignition, and k_1 and k_2 are constants. The time delay may be as little as a fraction of a second at higher temperatures or several minutes close to the auto-ignition temperature.

This effect may be of significance in flow systems where the fluid is a flammable mixture which comes in contact with a hot surface above the auto-ignition temperature but for a short time only.

16.2.4 Flashpoint

The flashpoint of a flammable liquid is the temperature at which the vapour pressure of the substance is such as to give a concentration of vapour in the air which corresponds to the lower flammability limit.

There are two methods of measuring flashpoint, the closed cup test and the open cup test. Some standard test methods are:

Closed cup	Pensky Martens	ASTM D 93–61 BS 2839: 1969
	Tagliabue	ASTM D 56–61
Open cup	Cleveland	ASTM D 92–57

The open cup flashpoint is usually a few degrees higher than the closed cup flashpoint. The relationships between vapour pressure, flammability limits, flashpoint and auto-ignition temperature are illustrated in Figure 16.8.

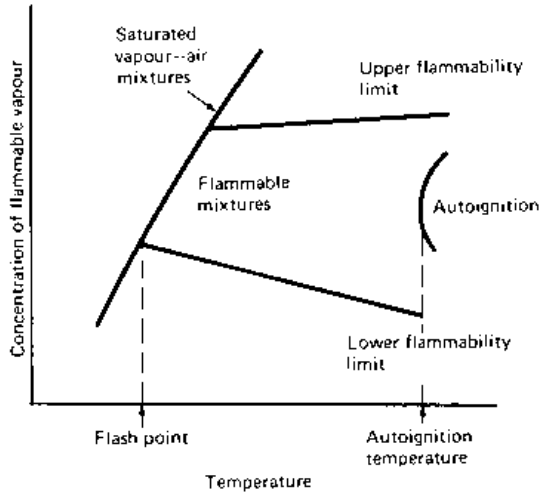


Figure 16.8 *Relationships between vapour pressure, flammability limits, flashpoint and auto-ignition temperature (after Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

A liquid which has a flashpoint below ambient temperature and can thus give rise to flammable mixtures under ambient conditions is generally considered more hazardous than one with a higher flashpoint. The flashpoint is a main parameter, therefore, in hazard classification of liquids and in government regulations based on these. Thus in aviation there has been movement to replace fuel JP4 with JP1. The former is akin to petroleum and has a low flashpoint, while the latter is more like kerosene and has a higher flashpoint, and is therefore safer.

Obviously, however, a higher flashpoint liquid also becomes more hazardous if it is heated up to a temperature above its flashpoint. The flashpoints of selected substances are given in Table 16.4.

16.2.5 Fire point

The fire point of a flammable liquid is the lowest temperature at which the liquid, when placed in an open container, will give off sufficient vapour to continue to burn when once ignited. The fire point is usually a few degrees above the open cup flashpoint.

16.2.6 Ignition energy

If a flammable gas–air mixture is to be ignited by a local source of ignition, however, it is not sufficient, as it is with auto-ignition, to raise a volume of the mixture to a certain temperature for a certain time. There is also a minimum volume of mixture so treated which is required in order to give rise to a continuing flame through the rest of the mixture. It has been shown, for example, that to ignite a methane–air mixture in a cold container by means of a hot patch an area of 18 mm^2 is required at 1000–1100°C (Rae, Singh and Danson, 1964). There is in effect an ignition energy requirement.

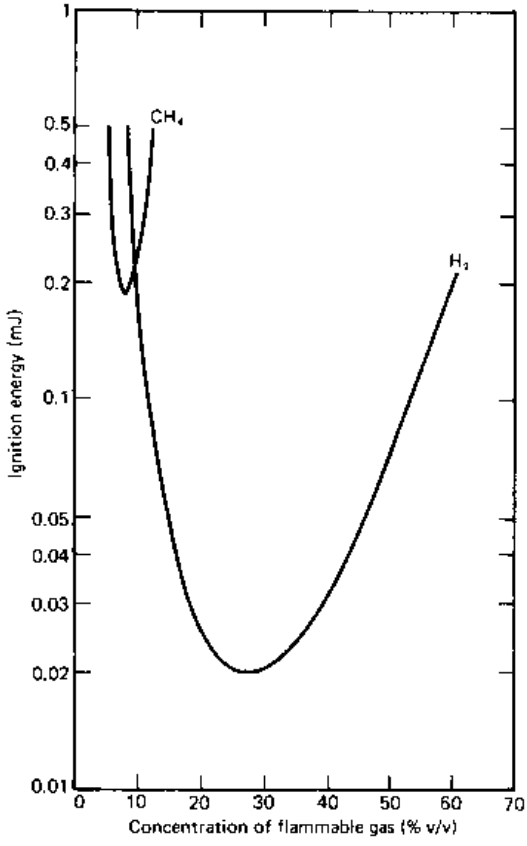


Figure 16.9 *Effect of mixture composition on electrical ignition energy of methane and of hydrogen in air (Factory Mutual Engineering Corporation, 1967)*

Similarly, ignition of a flammable gas–air mixture by a local source of ignition by electrical discharge occurs only if the latter possesses a certain energy. The variation of ignition energy with composition is shown for hydrogen and for methane in Figure 16.9.

There is a minimum ignition energy, which usually occurs close to the stoichiometric mixture. Minimum ignition energies for selected substances are shown in Table 16.6.

16.2.7 Burning velocity

The rate of combustion of a flammable mixture is affected by the burning velocity. The burning velocity is a property of the mixture. It is in effect the velocity at which a gaseous fuel–air mixture issuing from a burner burns back on to the burner. The burning velocity of a fuel–air mixture is usually determined by measurement of a premixed bunsen burner flame in the laminar region. The burning velocity S_u is obtained by dividing the volumetric gas flow V by the area A of the flame front cone:

$$S_u = V/A \qquad [16.2.6]$$

Alternatively, the burning velocity may be obtained from the velocity u of the gas and the half-angle α of the apex of the flame front cone:

$$S_u = u \sin \alpha \qquad [16.2.7]$$

If the flame front cone has radius r, height h and slant height l, the area A of the cone surface and the area A' of the cone triangular cross-section are, respectively

$$A = \pi r l \qquad [16.2.8a]$$

$$= \pi r (r^2 + h^2)^{\frac{1}{2}} \qquad [16.2.8b]$$

$$A' = rh \qquad [16.2.9]$$

Also

$$A = \pi A' l / h \qquad [16.2.10]$$

The gas velocity u is

$$u = \frac{V}{\pi r^2} \qquad [16.2.11]$$

The flame front is usually not a perfect cone and, in consequence, the equations just quoted are subject to errors of varying size. The choice of equations for the calculation of burning velocity is discussed by B. Lewis and von Elbe (1961) and by Fells and Rutherford (1969). The maximum burning velocity obtained at atmospheric pressure and temperature is referred to as the maximum fundamental burning velocity.

Burning velocities for methane in air and in oxygen are shown in Figure 16.10. In general, burning velocities for paraffinic hydrocarbons range from a few centimetres per second near the flammability limits up to about 45 cm/s near the stoichiometric mixture. For these hydrocarbons in oxygen the corresponding values are about 125 and 425 cm/s, respectively.

Burning velocities are affected by pressure and temperature. The effect of pressure changes is variable. A decrease in the burning velocity of stoichiometric methane–air mixtures has been found with increasing pressure in the range 0.5–20 atm, but with stoichiometric methane–oxygen mixtures an increase in pressure in the range 0.2–2 atm gave an increase in burning velocity.

Table 16.6 *Minimum ignition energies for selected substances in air*

	Minimum ignition energy (mJ)
Carbon disulphide	0.01–0.02
Hydrogen	0.019
Acetylene	0.02
Methane	0.29
Ethane	0.24
Propane	0.25
n-Butane	0.25
n-Hexane	0.25
Ethylene	0.12
Benzene	0.22
Ammonia	up to >100

Sources: Burgoyne (1965a); Factory Mutual Engineering Corporation (1967).

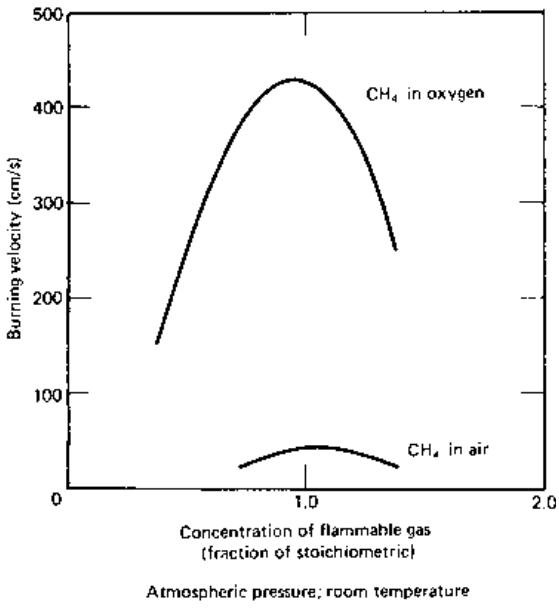


Figure 16.10 *Effect of mixture composition on burning velocity of methane in air and in oxygen (Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

The effect of temperature on burning velocity is more consistent and is sometimes described by the equation

$$S_u = A + BT^n \qquad [16.2.12]$$

where T is the absolute temperature, A and B are constants and n is an index. A value of 2.0 for the index n has been found for some paraffinic hydrocarbons (Zabetakis, 1965 BM Bull. 627, p. 43). Maximum fundamental burning velocities of selected substances in air and in oxygen are given in Table 16.7.

The actual flame speed in combustion of a flammable mixture is greater, and sometimes very much greater, than the burning velocity. Whereas the burning velocity is a property of the mixture only, the flame speed depends on other factors such as turbulence and pressure waves. If detonation occurs, the flame speed is greater by orders of magnitude than the burning velocity.

16.2.8 Adiabatic flame temperature

The heat radiated by combustion of a flammable mixture depends on the flame temperature, the theoretical maximum value of which is the adiabatic flame temperature. The adiabatic flame temperature is the temperature attained by combustion under adiabatic conditions. It is normally determined for the stoichiometric mixture and values quoted generally refer to this unless otherwise stated.

The adiabatic flame temperature can be calculated, but for an accurate calculation this is not entirely straightforward. Accounts of calculation methods are given by Hougen, Watson and Ragatz (1954–), W.A. Gray, Kilham and Müller (1976), Barnard and Bradley (1985), Drysdale (1985) and Kuo (1986).

The adiabatic flame temperature may be determined for constant pressure or constant volume conditions. The value normally quoted is for the former. For this case the enthalpy balance is

$$\Delta H_2 + \Delta H_1 + \Delta H_c = 0 \qquad [16.2.13]$$

or

$$\Delta H_2 = -\Delta H_1 + (-\Delta H_c) \qquad [16.2.14]$$

with

$$\Delta H_1 = \sum_{i=1}^{r} n_i \int_{T_1}^{T_o} c_{pi}(T)\,\mathrm{d}T \qquad [16.2.15]$$

$$= c_{pmr}(T_o - T_1) \qquad [16.2.16]$$

$$\Delta H_2 = \sum_{i=1}^{p} n_i \int_{T_o}^{T_2} c_{pi}(T)\,\mathrm{d}T \qquad [16.2.17]$$

$$= c_{pmp}(T_2 - T_o) \qquad [16.2.18]$$

where c_p is the specific heat at constant pressure of component i (kJ/kmol °C), c_{pm} is the mean specific heat over the range of interest (kJ/kmol °C), ΔH_c is the heat of combustion (kJ/mol of fuel), ΔH_1 is the enthalpy change between states 1 and 0 (kJ/kmol of fuel), ΔH_2 is

Table 16.7 *Maximum fundamental burning velocities of selected substances in air and in oxygen*

	Maximum fundamental burning velocity,[a] S_u	
	(cm/s)	(ft/s)
In air		
Methane	36.4[b]	1.2
Ethane	40.1	–
Propane	45[b]	1.5
n-Butane	40.5[b]	1.3
n-Hexane	38.5	1.3
Ethylene	68.8[b]	2.3
Town gas[c]	–	3.7
Acetylene	173	5.8
Hydrogen	320	11.0
Benzene	40.7[b]	–
In oxygen		
Methane	393[d]	–
Propane	390	–
Ethylene	550	–
Acetylene	1140	–
Hydrogen	1175	–

[a] The values given in the first column (cm/s) are those of Fiock (1955) and in the second column (ft/s) those of the HSE (1965 HSW Bklt 34). The values quoted from Fiock are for initial pressure atmospheric and initial temperature room temperature and, in most cases, dry gas, and generally are selected from several values listed.
[b] Some higher values are also listed by Fiock.
[c] For town gas containing 63% H_2.
[d] For stoichiometric mixture.

Table 16.8 *Constants for specific heat at constant pressure (Barnard and Bradley, 1985) (Courtesy of Chapman & Hall)*

Species	*Constant* [a]				*Valid over temperature range* (K)
	a	$10^2 b$	$10^5 c$	$10^9 d$	
H_2	29.09	−0.1916	0.4000	−0.870	273–1800
O_2	25.46	1.519	−0.7150	1.311	273–1800
N_2	27.32	0.6226	−0.0950	–	273–3800
CO	28.14	0.1674	0.5368	−2.220	273–1800
CO_2	22.24	5.977	−3.499	7.464	273–1800
H_2O	32.22	0.1920	1.054	−3.594	273–1800
CH_4	19.87	5.021	1.286	−11.00	273–1500
C_2H_2	21.80	9.208	−6.523	18.20	273–1500
C_2H_4	3.95	15.63	−8.339	17.66	273–1500
C_2H_6	6.895	17.25	6.402	7.280	273–1500
C_3H_8	−4.042	30.46	−15.71	31.71	273–1500
C_6H_6	−39.19	48.44	−31.55	77.57	273–1500
CH_3OH	19.04	9.146	−1.218	−8.033	273–1000
NH_3	27.55	2.563	0.9900	−6.686	273–1500
NO	27.03	0.9866	0.3223	0.3652	273–3800
SO_2	25.76	5.791	−3.809	8.606	273–1800

[a]Constants in the equation $c_p = a + bT + cT^2 + dT^3$, where c_p is the specific heat (kJ/kmol °C) and T is the absolute temperature (K).

Table 16.9 *Mean specific heats (kJ/kmol °C) at a constant pressure (after Hougen, Watson and Ragatz, 1954–)*

Final temperature, t (°C)	*Mean specific heat (kJ/kmol °C)*			
	O_2	N_2	CO_2	H_2O
2000	35.27	33.47	54.85	43.67
2100	35.42	33.61	55.14	44.05
2200	35.55	33.72	55.43	44.42

[a] Mean specific heat over the temperature interval 0°C to t°C. Values based on data for zero pressure given by the authors and based on those of Wagman (1953).

the enthalpy change between states 1 and 2 (kJ/kmol of fuel), n is the number of moles per mole of fuel, p is the number of products, r is the number of reactants and subscripts i, p and r denote component i, products and reactants, and 0, 1 and 2 denote the standard state, initial state and final state, respectively.

The specific heat c_{pi} of a reactant or product is a function of the temperature T. It is commonly represented in the form

$$c_{pi} = a_i + b_i T + c_i T^2 + d_i T^3 \qquad [16.2.19]$$

where a_i (kJ/kmol °C), b_i (kJ/kmol °C K), c_i (kJ/kmol °C K^2) and d_i (kJ/kmol °C K^3) are constants.

Then from Equations 16.2.17–16.2.19 the mean specific heat of product i is

$$c_{pmi} = \frac{\left(a_i T + b_i \frac{T^2}{2} + \frac{c_i T^3}{3} + \frac{d_i T^4}{4}\right)_{T_o}^{T_2}}{T_2 - T_o} \qquad [16.2.20]$$

and the mean specific heat of the product mixture is

$$c_{pmp} = \sum_{i=1}^{p} n_i c_{pmi} \qquad [16.2.21]$$

If necessary, equations similar to Equations 16.2.20 and 16.2.21, derived from Equations 16.2.15 and 16.2.19, may be used to obtain c_{pmr}, but generally the initial temperature T_1 is close to the standard temperature T_0 so that a point value of c_{pmr} may be used. If in fact $T_1 = T_0$, then $\Delta H_1 = 0$.

Table 16.8 gives values of the constants in Equation 16.2.19 for the determination of point values of the specific heats c_p. Table 16.9 gives values of the mean specific heat c_{pm} over the interval 0°C to t°C.

In the foregoing the implicit assumption is that the products of combustion are those given by the simple stoichiometric equation, which for hydrocarbons yields only CO_2 and H_2O. In fact, for flame temperatures above about 1370°C dissociation of the products of combustion occurs. At adiabatic flame temperatures, dissociation and ionization absorb a significant amount of energy and result in an appreciable lowering of the temperature of the flame. This is illustrated in Table 16.10, which shows that for propane the values obtained for the adiabatic flame temperature are 2219 K using a comprehensive set of equilibria, 2232 K using a simplified set and 2324 K considering only the formation of CO_2 and H_2O.

Calculations of the adiabatic flame temperature allowing for dissociation are complex. A computer program which performs such calculations has been described by Gordon and McBride (1971, 1976). An account of its use is given by Kuo (1986).

Table 16.11 gives some theoretical and experimental values of flame temperature quoted by B. Lewis and von Elbe (1987) and Siegel and Howell (1991). The theoretical values given in the table are adiabatic flame

Table 16.10 *Complete thermodynamic treatment of adiabatic flame temperature of propane in air (Barnard and Bradley, 1985) (Courtesy of Chapman & Hall)*

Species	*Concentration (mole fraction)*			
	Constant pressure			*Constant volume*
	Case 1	*Case 2*	*Case 3*	
CO_2	0.1004	0.1003	0.1111	0.0914
H_2O	0.1423	0.l439	0.1481	0.1374
N_2	0.7341	0.7347	0.7407	0.7276
CO	0.0099	0.0100		0.0182
H_2	0.0032	0.0033		0.0053
O_2	0.0048	0.0055		0.0075
NO	0.0020	0.0022		0.0052
CH_2O	$<10^{-5}$			$<10^{-5}$
C_2H_4	$<10^{-5}$			$<10^{-5}$
C_3H_6	$<10^{-5}$			$<10^{-5}$
N_2O	$<10^{-5}$			$<10^{-5}$
CHO	$<10^{-5}$			$<10^{-5}$
CH_3	$<10^{-5}$			$<10^{-5}$
C_2H_5	$<10^{-5}$			$<10^{-5}$
i-C_3H_7	$<10^{-5}$			$<10^{-5}$
H	0.0035			0.0009
O	0.0020			0.0008
N	$<10^{-5}$			$<10^{-5}$
OH	0.0027			0.0058
HO_2	$<10^{-5}$			$<10^{-5}$
Final temperature (K)	2219	2232	2324	2587

[a] Calculations are for a stoichiometric mixture. Case 1 refers to calculations based on a comprehensive set of equilibria, Case 2 to calculations using a smaller set of equilibria, and Case 3 to calculations made considering only the formation of CO_2 and H_2O.

Table 16.11 *Adiabatic flame temperatures of selected substances in air at atmospheric pressure*

	Theoretical[a] (K)		*Experimental* (K)	
	Complete combustion	*With dissociation and ionization*	*1*[a]	*2*[b]
Methane	2285	2191	2148	2158
Ethane	2338	2222	2168	2173
Propane	2629	2240	2198	2203
n-Butane	2357	2246	2168	2178
Ethylene	2523	2345	2248	2253
Propylene	2453	2323	2208	2213
Acetylene	2859			2598
Benzene	2484			
Carbon monoxide	2615			
Hydrogen	2490			2318

[a] Given by Siegel and Howell (1991), quoting Barnett and Hibbard (1957) and Gaydon and Wolfhard (1960). Values for combustion in dry air at 298 K.
[b] Given by B. Lewis and von Elbe (1987), quoting Loomis and Perrott (1928), G.W. Jones, Lewis and Seaman (1931) and G.W. Jones, Lewis, Friauf and Perrott (1931). See text.

temperatures at constant pressure. Details of the experimental temperatures are given in the footnote to the table. Lewis and von Elbe state that the experimental flame temperatures were probably influenced somewhat by heat loss and other factors, but that the error is small; Siegel and Howell describe the experimental values as 'maximum temperatures'.

16.2.9 Degree of flammability

Comparisons are often made between the flammability either of different substances or of different mixtures of the same substance in air. There is no single parameter which defines flammability, but some which are relevant are (1) the flashpoint, (2) the flammability limits, (3) the auto-ignition temperature, (4) the ignition energy and (5) the burning velocity.

The flashpoint of a substance is often treated as the principal index of flammability, a substance being regarded as highly flammable if it has a low flashpoint. The other flammability characteristics are also important, however. The flammability of the substance is increased by wide flammability limits and by a low minimum auto-ignition temperature, a low minimum ignition energy and a high maximum burning velocity.

The mixtures which have the lowest auto-ignition temperature and ignition energy and the highest burning

velocity, tend to occur near to, but normally not exactly at, the stoichiometric composition.

16.2.10 Quenching effects

Flame propagation is suppressed if the flammable mixture is held in a narrow space. Thus there is a minimum diameter for apparatus used for determination of flammability limits such that below this diameter the flammable range measured is narrower and inaccurate. Ultimately, if the space is sufficiently narrow, flame propagation is suppressed completely. The largest diameter as which flame propagation is suppressed is known as the quenching diameter. For an aperture of slot-like cross-section there is a critical slot width.

The term 'quenching distance' is used sometimes as a general term covering both quenching diameter and critical slot width and sometimes meaning the latter only. An account of quenching distances is given by Potter (1960). He gives the following empirical relation between quenching diameter D_o and critical slot width $D_\parallel$:

$$D_\parallel = 0.65 D_o \qquad [16.2.22]$$

He also discusses the effect of pressure and temperature on these variables.

There is a maximum experimental safe gap (MESG) which avoids the transmission of an explosion occurring within a container to a flammable mixture outside the container. The maximum experimental safe gap is measured in a standard apparatus. One apparatus consists of a spherical vessel with the gap between a pair of flat equatorial flanges, the breadth of the gap being 1 in. A value of less than 1 in. causes a decrease in the maximum experimental safe gap, but a greater value has no effect. An account of maximum safe gaps is given by Lunn and Phillips (1973).

Critical slot widths and maximum experimental safe gaps for selected substances in air are given in Table 16.12. It is emphasized that these values relate to a stationary flame. If the gas flow is in the direction of flame propagation, a smaller gap is needed to quench the flame and, conversely, if the gas flow is in the opposite direction, a larger gap will effect quenching. If the gas velocity is high enough, a condition can occur in which a flame propagating against the flow is stabilized at a constriction and causes local overheating.

For some substances, notably acetylene, carbon disulphide and hydrogen, the quenching diameters and distances are very small. These quenching effects are important in the design of flameproof equipment and of flame arresters.

Table 16.12 *Critical slot widths and maximum experimental safe gaps for selected substances in air*

	Critical slot width[a,b] (mm)	*Maximum experimental safe gap*[b,c] (mm)
Acetone	–	1.01
Acetylene	0.52	0.37[d]
Ammonia	–	3.18
Benzene	1.87	0.99
n-Butane	–	1.07[e]
Carbon disulphide	0.55	0.20
Carbon monoxide	–	0.91[d]
Cyclohexane	3.0	0.94
Ethane	–	0.91
Ethylene	1.25	0.65
Ethylene dichloride	–	1.82
Ethylene oxide	1.18	0.59
Hydrogen	0.50	0.20
Methane	2.16	1.14
n-Pentane	2.07	0.89[e]
Propane	1.75	0.92
Propylene	–	0.91
Vinyl chloride	–	0.96

Sources: Critical slot width: Potter (1960). Maximum experimental safe gap: Lunn and Phillips (1973), except as given in footnotes.

[a] Critical slot widths are for stoichiometric mixtures and are corrected where necessary to atmospheric pressure and 25°C.

[b] Where several values of critical slot width or maximum experimental safe gap are given in original reference, the value quoted here is the smallest.

[c] Maximum experimental safe gaps are corrected where necessary to atmospheric pressure and 20°C.

[d] Data for acetylene and carbon monoxide should be interpreted with care. For acetylene under certain ill-defined circumstances external ignitions have been reported at flange gaps too small to measure. For carbon monoxide data are for moist (not saturated) gas. Addition of moisture greatly increases the burning velocity of carbon monoxide.

[e] Burgoyne (1965a). Maximum experimental safe gap at atmospheric pressure.

16.2.11 Flammability in oxygen

The flammability of a substance depends strongly on the partial pressure of oxygen in the atmosphere. The oxygen concentration affects both the flammability

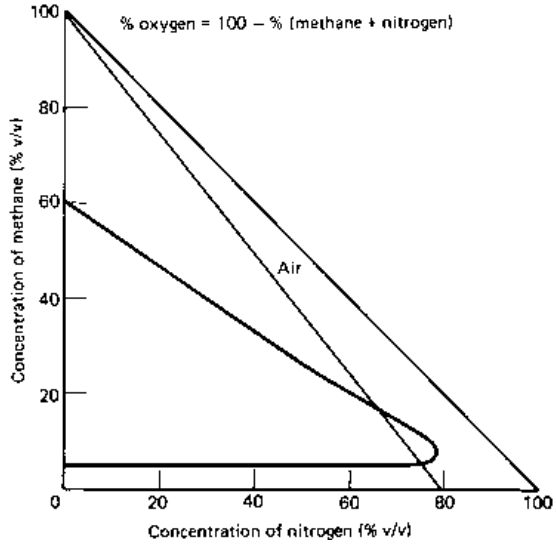


Figure 16.11 *Effect of oxygen concentration on flammability limits of methane (after Zabetakis, 1965 BM Bull. 627) (Courtesy of the Bureau of Mines)*

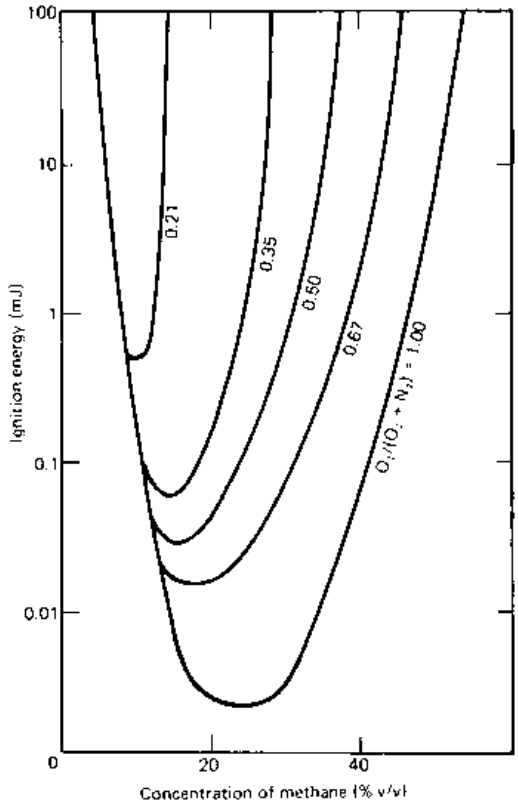


Figure 16.12 *Minimum spark ignition energies in methane–oxygen–nitrogen mixtures at 1 atm pressure (B. Lewis and von Elbe, 1961) (Courtesy of Academic Press)*

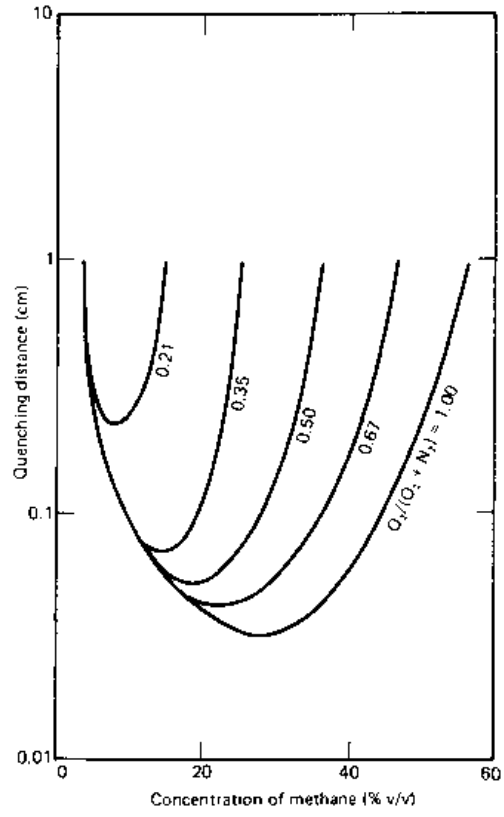


Figure 16.13 *Quenching distances in methane–oxygen–nitrogen mixtures at 1 atm pressure (B. Lewis and von Elbe, 1961) (Courtesy of Academic Press)*

Table 16.13 *Variability of experimental data on flammability characteristics in air*

Property	*Mixture*	*Value*	*Reference*
		(%v/v)	
Lower flammability limit (upwards propagation of flame)	Ethylene–air[a]	2.75	Jones *et al.* (1935 BM RI 3278)
		3.2	Burgoyne and Williams-Leir (1948a)
		3.3	Chapman (1921)
		(mJ)	
Minimum ignition energy	Ammonia–air[b]	40	Magison (1966)
		60	Magison (1966)
		< 90	G.F.P. Harris and MacDermott (1977)
		170	G.F.P. Harris and MacDermott (1977)
		680	Buckley and Husa (1962)
		(°C)	
Autoignition temperature	Acetone–air[c]	465	Zabetakis (1965 BM Bull. 627)
		600	Marsden (1963)
	Methanol–air[c]	385	Zabetakis (1965 BM Bull. 627)
		470	Marsden (1963)
	Methylethyl[c] ketone–air	404	Hilado and Clark (1972a)
		550	Marsden (1963)

[a] The value given by Zabetakis (1965 BM Bull. 627) and in the ICI *Electrical Installations Code* (ICI/RoSPA 1972 IS/91) is 2.7%.
[b] These differences are discussed by G.F.P. Harris and MacDermott (1977).
[c] These differences have been noted by Santon (1977).

limits and the other flammability parameters. In general, increasing oxygen content alters the lower flammability limit only slightly, but its effect on the upper flammability limit is marked. Figure 16.11 illustrates the effect of oxygen concentration on the flammability limits of methane–oxygen–nitrogen mixtures. Conversely, there is a minimum oxygen content to support combustion. For the system shown in Figure 16.11 this is approximately 12%. Increasing the oxygen content reduces the ignition energy and the quenching distance of methane–oxygen–nitrogen mixtures as shown in Figures 16.12 and 16.13, respectively. Again the effect is a marked one.

The increase in burning velocity of methane when air is replaced by oxygen was illustrated in Figure 16.10.

16.2.12 Uncertainty in data

It has already been emphasized that there is frequently some uncertainty in the data available for design. The point is illustrated by the data on flammability characteristics given in Table 16.13. The lower flammability limit of ethylene–air mixtures at atmospheric pressure and temperature is generally taken as 2.7%, as indicated in the table, and it is not regarded as particularly uncertain. But as the figures show, previous values differ from this by a factor as high as 1.22. On the other hand, the minimum ignition energy of ammonia–air mixtures at atmospheric pressure and temperature appears still to be subject to some uncertainty. The situation is similar for the auto-ignition temperature of acetone, methanol and methylethyl ketone mixtures with air at atmospheric pressure.

16.3 Combustion Phenomena

The use of the flammability characteristics just described is a simplification of rather complex combustion phenomena, which for engineering purposes it is necessary to make. It is convenient at this point, therefore, to indicate some of this combustion background, both as a commentary on the flammability characteristics just described and as an introduction to the subsequent sections on flames and fires.

Accounts of basic combustion are given in *The Science of Flames and Furnaces* (Thring, 1952), *Flames, Their Structure, Radiation and Temperature* (Gaydon and Wolfhard, 1953–), *Some Fundamentals of Combustion* (Spalding, 1955), *Combustion, Flames and Explosions of Gases* (B. Lewis and von Elbe, 1961, 1987), *Combustion Theory* (F.A. Williams, 1965), *Fundamentals of Combustion* (Strehlow, 1968a), *Flames and Combustion Phenomena* (J.N. Bradley, 1969), *Flame and Combustion* (Barnard and Bradley, 1985), *An Introduction to Fire Dynamics* (Drysdale, 1985), *Principles of Combustion* (Kuo, 1986) and *Combustion of Liquid Fuel Sprays* (A. Williams, 1990).

Selected references on combustion phenomena are given in Table 16.14. Some topics in combustion research relevant to loss prevention are shown in Table 16.15.

In this section the following aspects of combustion are reviewed:

(1) flame propagation;
(2) diffusion and premixed flames;
(3) premixed flame flashback and blowoff;
(4) diffusion flame characteristics;
(5) flame stretch and wrinkling;
(6) reaction kinetics and transport processes;
(7) thermal explosion theory;
(8) flammability limits;
(9) ignition phenomena;
(10) burning velocity;
(11) quenching effects;
(12) cool flames;
(13) combustion in tubes.

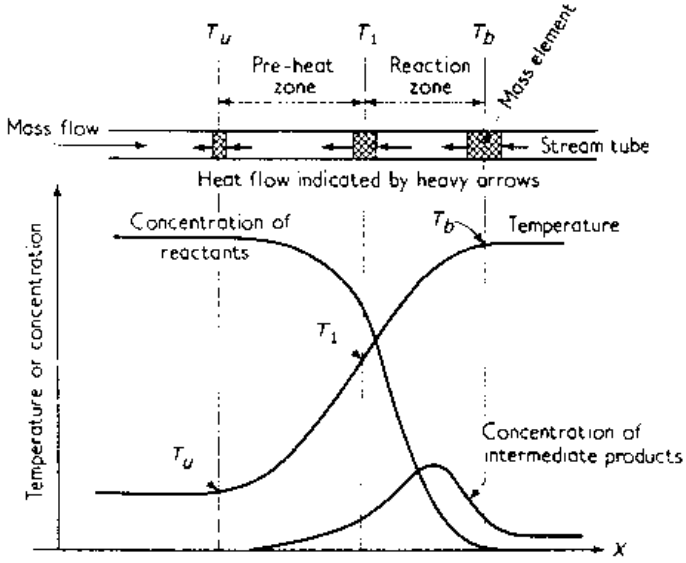


Figure 16.14 *Scheme of a planar combustion wave (B. Lewis and von Elbe, 1961) (Courtesy of Academic Press)*

Table 16.14 *Selected references on combustion, pre-flame and ignition phenomena, slow oxidation and cool flames, and flame propagation*

Perkin (1882); Lotka (1920); Fenning (1926); J. White (1927); Payman (1928); Prettre, Dumanois and Lafitte (1930); Norrish (1935); Pease (1935, 1937); Ubbelohde (1935, 1936); Norrish and Foord (1936); Coward and Payman (1937); von Elbe and Lewis (1937a,b); Newitt (1937); Newitt and Thornes (1937); Townend (1937); Hsieh and Townend (1939a–c); Townend and Hsieh (1939); B. Lewis and von Elbe (1947); Boord (1949); Henkel, Hummel and Spaulding (1949); Henkel, Spaulding and Hirschfelder (1949); Hirschfelder and Curtiss (1949); Prettre (1949); Reynolds and Gerstein (1949); Spence and Townend (1949); Jost (1950); Fenn (1951); Grove and Walsh (1953); J.E. Johnson, Crellin and Carhart (1953, 1954); Schmidt, Steinecke and Neubert (1953); G.K. Adams and Scrivener (1955); Bardwell (1955); Bawn and Skirrow (1955); Dugger, Weast and Heimel (1955); Foresti (1955); Grumer (1955); Newitt (1955); Burgoyne and Weinberg (1956); Barnett and Hibbard (1957); von Karman (1957); Lucquin and Laffitte (1957); W.W. Robertson and Matsen (1957); Tipper (1957); D.H. Allen *et al.* (1959); Berlad and Yang (1959, 1960); Ferguson and Yokley (1959); Goldenberg and Pelevin (1959); Mullins and Penner (1959); Salooja (1960, 1961, 1964a,b, 1966, 1967, 1968a,b); Wolfhard and Bruszak (1960); Barnard and Hawtin (1961); Yang (1962); Hirschfelder (1963); Seakins and Hinshelwood (1963); Rhein (1964); Yao and Ruof (1964); Agnew and Agnew (1965); Barnard and Ibberson (1965); Bonner and Tipper (1965a,b); Sueyasu and Hikita (1965); Adler and Zaturska (1966); Fish (1966, 1968); Melvin (1966, 1969a,b); Ashmore (1967); Ashmore and Preston (1967); Barnard and Kirschner (1967); Hoare, Ting-Man Li and Walsh (1967); Knox (1967a,b); Barnard and Sankey (1968); Bell, Skirrow and Tipper (1968); M.H. Friedman (1968); J.F. Griffiths, Skirrow and Tipper (1968–); Howe and Ting-Man Li (1968); Neiman and Gal (1968); Barnard and Watts (1969, 1972); Fish *et al.* (1969); B.F. Gray (1969a,b); Bowman (1970); Fine, Gray and Macinven (1970); R. Hughes and Simmons (1970); Korman (1970); Perche, Perez and Lucquin (1970, 1971); Dechaux, Flament and Lucquin (1971); Drysdale (1971); Halstead, Prothero and Quinn (1971, 1973); Knox and Kinnear (1971); Leyer and Manson (1971); Meyer and Oppenheim (1971a,b); Burgess and Laughlin (1972); Crossley *et al.* (1972); Lucquin and Antonik (1972); H. Phillips (1972a, 1973); Tse (1972); Barnard and Harwood (1973a,b, 1974); Berlad (1973); Dehn (1973); Luckett and Pollard (1973); Feay and Bowen (1973); R. Hughes and Prodan (1973); Vovelle and Delbourgo (1973); McKay *et al.* (1975); F.W. Williams, Indritz and Sheinson (1975); D.C. Bull, Pye and Quinn (1976); Caprio, Insola and Lignola (1977); Hirano *et al.* (1977); Bilger (1979); Dechaux and Delfosse (1979); Maly and Vogel (1979); Affens and Sheinson (1980); Coffee (1980, 1982b); Kolodner and Pratt (1980); d'Onofrio (1980); Abdel-Gayed and Bradley (1981); Coffee (1981 LPB 81); Snee (1981 LPB 81); Hoffmann-Berling, Günther and Leuckel (1982); Rhee (1982); F.A. Williams (1982, 1992); G. Freeman and Lefebvre (1984); Ronney (1985); Chakir *et al.* (1989); Wilk *et al.* (1989); Xiao-Jing Wang (1989); Sloane (1990a,b, 1992); Borghese *et al.* (1991); P.P. Gray (1991); B.F. Gray, Merkin and Griffiths (1991); Leclerc-Battin *et al.* (1991); Pitt, Clements and Topham (1991); Battin-Leclerc *et al.* (1992); D. Bradley (1992); B.F. Gray, Little and Wake (1992); Miles and Gouldin (1992); Trevino and Mendez (1992); Sloane and Ronney (1993); Vanpee (1993)

Chemical reaction kinetics

Kassel (1937); Dugleux and Freling (1955); von Elbe (1955); Hoare and Walsh (1955); Levy (1955); Ubbelohde *et al.* (1955); Vanpee and Grard (1955); Giddings and Hirschfelder (1957); W.G. Parker (1958); Szabo (1959); Baulch *et al.* (1973); Jensen and Jones (1978); Lovachev (1981); Westbrook and Dryer (1981); Kaufman (1982); Golden and Larson (1985); Wolfrum (1985); R.D. Levine (1989); Stewart, Rothem and Golden (1989); Troe (1989); Hai Wang and Frenklach (1991)

Kinetic schemes: Dixon-Lewis (1955); W.W. Robertson *et al.* (1955); Westbrook, Hellwig and Anderson (1955); Knox (1959, 1967a); Minkoff and Tipper (1962); Ashmore, Dainton and Sugden (1967); Smoot, Hecker and Williams (1976); Dryer and Schug (1982); J.A. Miller *et al.* (1982); Westbrook and Pitz (1984); Warnatz (1985); Hwang *et al.* (1987); Yetter, Dryer and Rabitz (1991)

Some of the reviews are essentially historical, illustrating the development of the basic concepts.

16.3.1 Flame propagation

A useful starting point for consideration of combustion is the propagation of the flame as an adiabatic planar combustion wave, as shown in Figure 16.14. At the front of the combustion zone the temperature is that of the burnt gas T_b. From this maximum value the temperature then falls off. Within the wave there is a plane at temperature T_1 where transition occurs from a heat source to a heat sink in that the heat supplied by the reaction now falls below the heat lost to the unburnt gas behind. The temperature then falls further until it reaches the temperature T_u of the unburnt gas behind the wave. The first part of the combustion zone, in front of T_1, is the reaction zone and the second part, behind T_1, the preheat zone.

In many practical situations the flame front is not planar. In particular, a small spherical flame has a divergent flame front and undergoes stretch, as described below. However, as the spherical flame becomes larger, the flame front may be approximated by a planar front.

Although it is convenient to start with the model of the adiabatic planar combustion wave, it has often been the case in combustion theory that progress has only been made when this model is abandoned and real, but more complex, situations are considered. Thus B. Lewis and von Elbe (1961) state:

> The use of the adiabatic plane wave equations for general theoretical deductions of flame behaviour is futile because the model is unrealistically restricted by the specification of one-dimensional, adiabatic propagation in an infinite medium for an infinite time. For one thing, the model does not yield limits of inflammability as they are known to the experimenter. (p. 210)

Table 16.15 *Some topics in combustion research relevant to loss prevention*

- Chemical kinetics of combustion
- Combustion initiation and propagation:
  - Flammability limits
  - Ignition phenomena
    - Spontaneous ignition
    - Spark ignition
    - Hot wire ignition
    - Hot surface ignition
    - Hot gas ignition
    - Hot particle ignition
    - Compression ignition, shock heating
    - Induction period
  - Flame propagation
  - Slow oxidation, cool flames
  - Quenching effects
    - Burning velocity
    - Measurement methods
    - Turbulence effects
- Detonation:
  - Properties of detonation wave
  - Detonation limits
  - Detonation cell structure
  - Transition from deflagration to detonation
  - Detonation in tubes
  - Detonation in vapour clouds
- Flames:
  - Premixed flames
  - Diffusion flames
  - Flame stability, flashback, blowoff
  - Flame stretch and wrinkling
  - Flame emissivity
    - Emissivity of CO_2, H_2O
    - Emissivity of sooty flames
    - Soot formation and properties
- Inerting
- Inhibition
- Flame spread:
  - Flame spread over solid surfaces
  - Flame spread over liquid pools
- Ignition and burning of wood and cellulose:
  - Calorific value of wood
  - Thermal radiation levels for spontaneous and pilot ignition
  - Burning of wood
  - Wood crib fires
- Duct fires
- Pool fires:
  - Flame dimensions
  - Flame emissivity
  - Heat transfer to pool
  - Regression rate
- Large fires
- Vapour cloud fires and explosions
- Mist and spray combustion and explosion:
  - Burning of single drops
  - Burning of mist/spray clouds
- Dust fires and explosions:
  - Dust explosibility limits
  - Dust cloud explosions
  - Smouldering dust fires
- Self-heating, thermal explosion
- Building fires

An important feature in combustion work is the flow regime. In particular, there is a distinction between a flame propagating in a stagnant gas and in a flowing gas. Another distinction is that between laminar and turbulent flow. Flammability characteristics such as the ignition energy or burning velocity are affected by the flow regime.

16.3.2 Diffusion and premixed flames

A fundamental distinction is made between (1) premixed flames and (2) diffusion flames. In a premixed flame the air for combustion is mixed with the fuel gas before it issues from the orifice, while in a diffusion flame gas or liquid leaving the orifice is pure fuel and the air for combustion has to diffuse to it from the surrounding atmosphere. Both types of flame may be produced on a bunsen burner, a premixed flame being obtained by opening the primary air inlet and a diffusion flame by closing it.

With a premixed flame the rate of burning is limited by reaction kinetics, whilst, in principle, with a diffusion flame the rate limiting mechanism is diffusion. At high turbulence in a diffusion flame, however, kinetics and diffusion may be of roughly equal importance.

Another distinction in flames is that between (1) laminar flames and (2) turbulent flames. The criterion for transition from the laminar to the turbulent regime in a flame is the Reynolds number. The relevant Reynolds number, however, is that of the flame, which is actually several times less than that of the cold gas leaving the tube, because the gas viscosity at the flame temperature is that much greater.

16.3.3 Premixed flame flashback and blow-off

The behaviour of a premixed flame burning on a tube or similar burner is a function of the concentration of the fuel and of the gas velocity. Aspects of particular interest are flashback, blow-off, lift and blow-out of the flame. These features have been studied for flames of butane–air mixture by Wohl, Kapp and Gazley (1949) and are shown in Figure 16.15. In region A a stable flame can exist only at the burner port and in region B only lifted off the port. In region C the flame may be stable either on the port or lifted off it. In region D flashback can occur down the burner pipe.

The limits for flashback, blow-off and lift are determined by the velocity gradients at the boundary of the flame. In the flame the gas velocity is opposed by the axial component of the burning velocity. Flashback occurs under conditions where the gas velocity is low relative to the burning velocity. Blow-off at lower fuel concentration and lift at high fuel concentrations occur where the gas velocity is high relative to the burning velocity. The lift curve is an extension of the blow-off curve. The limits for blow-out and drop back of a lifted flame are not determined by the boundary velocity gradients and their shapes are specific for each burner diameter.

For laminar flow, from the Poiseuille equation the boundary velocity gradient g is

$$g = 4V/\pi r^3 \qquad [16.3.1]$$

where r is the distance from the centre of the tube to the boundary of the stream and V is the volumetric flow

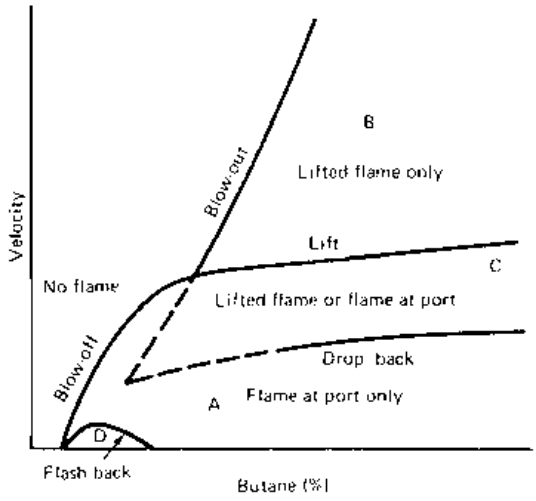


Figure 16.15 *Scheme of characteristic regions of flame stability for a premixed flame (after Wohl, Kapp and Gazley, 1949) (Courtesy of the Combustion Institute)*

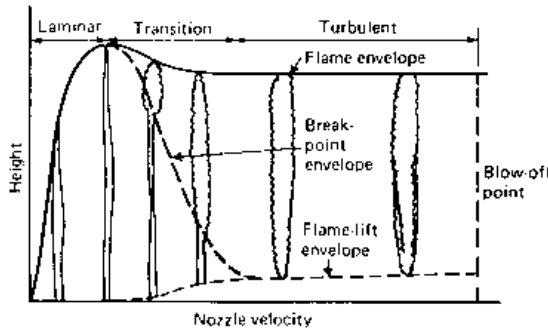


Figure 16.16 *Scheme of characteristic regions of flame stability for a diffusion flame (after Hottel and Hawthorne, 1949; Gugan, 1976) (Courtesy of the Combustion Institute and the Institution of Chemical Engineers)*

of gas. The critical boundary velocity gradient for flashback g_F may be obtained from Equation 16.3.1 using the volumetric flow for flashback V_F. Likewise, the critical boundary velocity gradient for blow-off g_B may be obtained using the volumetric flow for blow-off V_B.

Data on critical velocity gradients for flashback and for blow-off have been given by M.E. Harris, Grumer, von Elbe and Lewis (1949).

16.3.4 Diffusion flame characteristics

The behaviour of a diffusion flame is a function of the fuel velocity. As aspect of particular interest is the dimensions of the flame. This is illustrated in Figure 16.16, which is based on the work of Hottel and Hawthorne (1949) and a further interpretation by Gugan (1976). In the laminar regime the flame length is approximately proportional to the velocity, while in the turbulent regime it is independent of velocity. Turbulence spreads from the flame tip downwards. As velocity increases there are successively a region where the flame may be on the port or lifted, a region where only a lifted flame occurs and a point beyond which there is blow-off.

There are a number of correlations for the dimensions of a diffusion flame. The simple equation given by Jost (1946) for flame length is

$$L = \frac{d^2 u}{4D} \qquad [16.3.2]$$

where d is the diameter of the pipe (m), D is the diffusion coefficient (m^2/s), L is the flame length (m), and u is the fuel velocity (m/s).

For the laminar regime the diffusion coefficient D may be taken as the molecular diffusion coefficient D_m, which is a constant with respect to velocity. The flame length in this regime is thus proportional to velocity. But for the turbulent regime, D may be taken as the eddy diffusion coefficient D_e, which is proportional to the velocity u. The flame length in this regime is thus independent of velocity.

For the turbulent regime an equation commonly used to predict flame length is that of Hawthorne, Weddell and Hottel (1949):

$$L = \frac{5.3D}{C_t}\left\{\frac{T_f}{\alpha_t T_n}\left[C_t + (1 - C_t)\frac{M_s}{M_n}\right]\right\}^{\frac{1}{2}} \qquad [16.3.3]$$

where C_t is the concentration of fuel in the stoichiometric mixture (mole fraction), D is the diameter of the pipe (m), L is the flame length (m), M_n is the molecular weight of the fuel, M_s is the molecular weight of the surrounding fluid (normally air), T_f is the absolute adiabatic flame temperature (K), T_n is the absolute temperature of fuel in the pipe (K), and α_t is the ratio of the number of moles of unreacted and reacted gas in the stoichiometric mixture.

The shape of the flame envisaged in this treatment is an inverted cone with the apex at the orifice such that

$$\frac{L}{D} = 5.3\frac{W}{D} \qquad [16.3.4]$$

where W is the diameter at the top of the flame (m).

Another equation for the diameter of the flame is given by Baron (1954):

$$Z = 0.29x[\ln(L/x)]^{\frac{1}{2}} \qquad [16.3.5a]$$

and

$$Z_{max} = 0.12L \qquad \text{at} \qquad x = 0.61L \qquad [16.3.5b]$$

where x is the axial distance (m), Z is the flame diameter (m) and the subscript max denotes the maximum.

16.3.5 Flame stretch and wrinkling

Two properties of the laminar combustion wave which are of particular importance in combustion theory are flame stretch and flame wrinkling. If a combustion wave enters a flow field where there are significant changes of velocity over a distance comparable with the width η_o of the wave, significant stretching of the flame occurs. If a flow line of velocity U intersects the T_1 surface of the wave, as shown in Figure 16.17, the velocity of the flow line at a distance η_o along the line normal to this surface

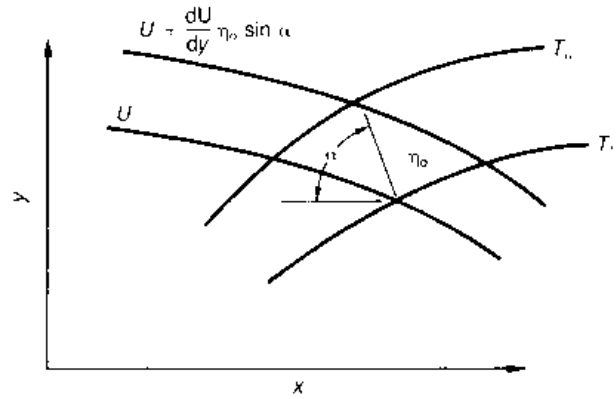


Figure 16.17 *Scheme of stretch of combustion wave in a flow field (after B. Lewis and von Elbe, 1961) (Courtesy of Academic Press)*

at the point of intersection is $U + (\mathrm{d}U/\mathrm{d}y)\eta_o \sin\alpha$. The ratio of the mass flows normal to this surface over the distance η_o is $1 + (\mathrm{d}U/\mathrm{d}y)(\eta_o/U) \sin\alpha$ and where the flow velocity is much greater than the burning velocity this reduces to $1 + (\mathrm{d}U/\mathrm{d}y)(\eta_o/U)$. The fractional increase, or stretch, is thus

$$\frac{\mathrm{d}U}{\mathrm{d}y}\frac{\eta_o}{U} = K \qquad [16.3.6]$$

where K is the Karlovitz number, which is thus a measure of the flame stretch.

The parameter η_o may be obtained from the heat balance in the combustion wave:

$$c_p \rho_u S_u (T_1 - T_u) = k\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_1 \qquad [16.3.7]$$

The distance η_o is taken as

$$\eta_o = (T_1 - T_u)/(\mathrm{d}T/\mathrm{d}x)_1 \qquad [16.3.8]$$

Then from Equations 16.3.7 and 16.3.8

$$\eta_o = k/c_p \rho_u S_u \qquad [16.3.9]$$

where c_p is the specific heat, S_u is the fundamental burning velocity, ρ is the density, k is a constant and the subscript u denotes unburnt gas.

If the flame stretch is sufficiently great, the flame is quenched. The Karlovitz number K, as a measure of flame stretch, is therefore also a criterion of quenching.

The Karlovitz number K may also be defined in terms of the critical velocity gradient for blow-off. The definition is

$$K = g_B \eta_o / S_u \qquad [16.3.10]$$

The flame stretch concept may also be applied to a spherical combustion wave in stagnant gas. If a sphere diameter d of burnt gas exists with an unburnt outer shell thickness η_o, the ratio of the surface areas after and before combustion of this shell is

$$= \frac{\pi(d + 2\eta_o \rho_u/\rho_b)^2}{\pi d^2} \qquad [16.3.11]$$

$$\approx 1 + 4\eta_o \rho_u / d\rho_b \qquad [16.3.12]$$

The fractional flame stretch is then

$$K = 4\eta_o \rho_u / d\rho_b \qquad [16.3.13]$$

Critical values of K for spark ignition are given by B. Lewis and von Elbe (1961) and lie mainly in the range 0.5–1.5.

If in the combustion wave of a stoichiometrically unbalanced mixture the diffusivity of the deficient component substantially exceeds that of the excess component, the gas mixture entering the wave stratifies so that there are alternate increases and decreases in the burning velocity. The wave becomes wrinkled and exhibits a cellular structure.

16.3.6 Reaction kinetics and transport processes

At the most fundamental level the process of combustion is governed by chemical reaction and transport processes. There are available reaction kinetic schemes for the reaction of many of the main compounds of interest.

Certain reactions have proved of particular interest to investigators. Semenov (1935), for example, discusses the reactions of oxygen with hydrogen, carbon monoxide and hydrocarbons and of hydrogen with chlorine and bromine. B. Lewis and von Elbe (1961) also discuss the reactions of oxygen with hydrogen, carbon monoxide and hydrocarbons and those in the H_2–CO–O_2 system. The reactions in the hydrogen–bromine systems have been of particular interest, as discussed by Lovachev *et al.* (1973).

16.3.7 Thermal explosion theory

Many problems in combustion involve the self-heating of a reactive mass in a defined volume. The theory which deals with this, thermal explosion theory, or simply thermal theory, is therefore important in combustion and has numerous applications.

The concept of thermal explosion derives from Van't Hoff (1884), who identified the condition for thermal ignition as one in which no equilibrium between the reacting system and its surroundings can exist. This was developed qualitatively by Le Chatelier (1937), who characterized the problem as one in which the variation of heat production is a curve and that of heat loss is a

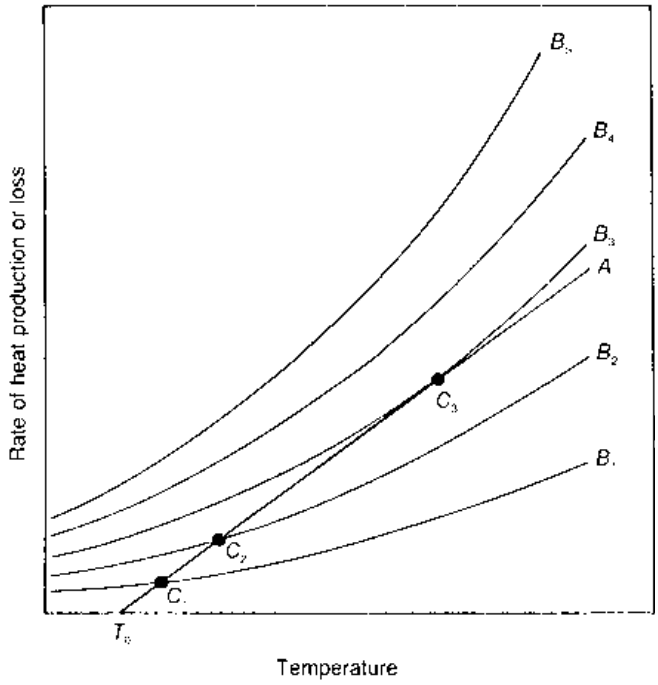


Figure 16.18 *Heat generation by and removal from a chemical reaction (after Semenov, 1935; Knox, 1967a)*

straight line, as illustrated in Figure 16.18. A quantitative treatment of thermal explosion theory was described in *Chemical Kinetics and Chain Reactions* by Semenov (1935), and developed by Semenov, Frank-Kamenetsky and Zeldovich (e.g. Zeldovich and Frank-Kamentsky, 1938; Frank-Kamenetsky, 1939a,b; Semenov, 1940). Accounts of thermal explosion theory are given in *Diffusion and Heat Exchange in Chemical Kinetics* (Frank-Kamenetsky, 1955) and *Selfheating: Evaluating and Controlling the Hazards* (Bowes, 1984) and by P. Gray and Lee (1967b) and Merzhanov and Averson (1971).

The basic concepts of thermal explosion theory are as follows. For a mass subject to an exothermic reaction the unsteady-state heat balance is

$$c\rho\frac{\partial T}{\partial t} = k\nabla^2 T + Q \qquad [16.3.14a]$$

$$= k\left[\frac{\mathrm{d}^2T}{\mathrm{d}x^2} + \frac{\mathrm{d}^2T}{\mathrm{d}y^2} + \frac{\mathrm{d}^2T}{\mathrm{d}z^2}\right] + Q \qquad [16.3.14b]$$

with

$$Q = Q'\rho A \exp(-E/RT) \qquad [16.3.15]$$

where A is the pre-exponential factor, c is the specific heat of the reacting mass, E is the activation energy, k is the thermal conductivity, Q is the heat released per unit volume, Q' is the heat of reaction per unit mass, t is the time, T is the absolute temperature, x, y and z are the distances from the centre of the hot spot in the x, y, and z directions, respectively, ρ is the density and ∇^2 the Laplacian operator with respect to the distance x.

The exponential term in Equation 16.3.15 may be approximated as follows:

$$\exp(-E/RT) \approx \exp\{-(E/RT_o)[1-(T-T_o)/T_o]\} \qquad [16.3.16]$$

$$= \exp(-(E/RT_o)\exp[(E/RT_o^2)(T-T_o)] \qquad [16.3.17]$$

where T_o is the initial temperature.

A dimensionless parameter θ is defined as

$$\theta = \frac{E}{RT_o^2}(T-T_o) \qquad [16.3.18]$$

Substituting from Equation 16.3.18 in Equation 16.3.17 gives

$$\exp(-E/RT) = \exp(-E/RT_o)\exp\theta \qquad [16.3.19]$$

Another dimensionless parameter δ is defined as

$$\delta = \frac{Q'\rho A r^2}{k}\frac{E}{RT_o^2}\exp(-E/RT_o) \qquad [16.3.20]$$

where r is the semi-thickness or radius of the reacting volume.

Then, defining two further dimensionless parameters

$$\zeta = x/r \qquad [16.3.21]$$

$$\tau = \frac{kt}{c\rho r^2} \qquad [16.3.22]$$

Equation 16.3.14 becomes, in dimensionless form,

$$\frac{d\theta}{d\tau} = \nabla^2\theta + \delta \exp\theta \qquad [16.3.23]$$

where ∇^2 is now the Laplacian operator with respect to ζ.

From Equation 16.3.14 the following equation for the temperature may be obtained for particular geometries:

$$c\rho\frac{dT}{dt} = k\left[\frac{d^2T}{dx^2} + \frac{m}{x}\frac{dT}{dx}\right] + Q \qquad [16.3.24]$$

or, in dimensionless form,

$$\frac{d\theta}{d\tau} = \frac{d^2\theta}{d\zeta^2} + \frac{m}{\zeta}\frac{d\theta}{d\zeta} + \delta \exp\theta \qquad [16.3.25]$$

where $m = 0$, 1 or 2 for a slab, cylinder or sphere, respectively.

There are numerous assumptions which may be made concerning the geometry, the boundary conditions, the physical properties and the reaction kinetics of the thermal explosion problem and there are numerous applications of the theory. This has given rise to a large literature.

The application of the thermal explosion model to combustion problems is considered in this section, while its application to self-heating of solid materials is discussed in Section 16.6.

16.3.8 Flammability limits

It is convenient for design purposes to define flammability limits, but the question of whether such flammability limits are a fundamental physicochemical property has been the subject of some debate. Reviews of the fundamentals of flammability limits have been given by Egerton (1953), B. Lewis and von Elbe (1961), Lovachev *et al.* (1973), Lovachev (1979) and Macek (1979).

The determination of practical flammability limits is usually effected using the Bureau of Mines apparatus as described by Coward and Jones (1952 BM Bull. 503). In this apparatus it is found that the lower limit concentration is lower and the upper limit concentration is higher for upward than for downward propagation. Since for design purposes it is desirable to use the wider limits, Coward and Jones recommend the use of the flammability limits for upward propagation.

In his review Egerton states three conditions which a satisfactory theory of flammability limits should meet. It should predict (a) the existence of a lower limit, (b) the value of the lower limit concentration and (c) the value of the burning velocity at the lower limit. He discusses the relation between the flammability limit and the flame temperature attained at the limit.

Egerton and Powling (1948) have drawn attention to the relationship which exists, given complete combustion, between the lower and upper limits if a limit mixture requires a certain concentration of fuel to provide the temperature necessary for flame propagation. Provided allowance is made for the different specific heats of the two mixtures, the upper limit might then be estimated from the lower one. This approach is applicable only if combustion is complete. This is not the case for hydrocarbon–air mixtures.

For the upper flammability limit Egerton and Powling found the principal determining factor to be the heat of combustion per mole of mixture. Egerton states that the direction of propagation is important because of the effect of convection. The upward propagating flame is assisted by convection.

It is desirable to have some more fundamental method of measuring flammability limits than the standard tube method. Such a method is the flat flame method described by Egerton and Thabet (1952). This method appears better suited to the provision of fundamental data than the standard method, although it is not suggested that it should replace the latter for practical determinations. Egerton (1953) presents data on the different limit flame temperatures obtained by the standard tube and flat flame methods, as shown in Table 16.16. The temperature given by the latter is lower and more constant.

Spalding (1957d) has presented a theory of flammability limits. He argues that a theory which is capable of predicting the existence of a limit of flammability needs to take account of heat loss. The novel feature of his theory is that it allows for heat loss by radiation. The theory for the laminar one-dimensional flame is thus brought into line with the theoretical treatments of other types of flame, each of which exhibits a zone of stable operation limited on one side by chemical kinetics and on the other by heat loss to the surroundings. The theory is not dependent on any particular assumptions about the dependence of the reaction rate on concentration and temperature, other than that the dependence of the rate should be steeper than that for the heat transfer. Spalding found that at the flammability limit there is a small but finite burning velocity. In addition, he showed that there exist two burning velocities, of which only the upper one is stable in normal circumstances.

Other workers who have given theories of flammability limits based on heat radiation include Zeldovich (1941) and Rozlovsky (1970). Later workers have tended to argue that the heat radiation theory is difficult to reconcile with experimental phenomena. The work of Egerton and Powling (1948), showing that heat radiation loss is small, is often quoted.

Table 16.16 *Flammability limits: lean limit flame temperatures from standard tube and flat flame methods (after Egerton, 1953) (Courtesy of the Combustion Institute)*

Gas	*Lower limit*	*Flame temperature* (°C)	
	(%)	*Tube method*	*Flat flame method*
Methane	5.26	1254	1222
Propane	3.10	1383	1200
n-Butane	1.93	1445	1233
n-Pentane	1.62	1485	1158
n-Heptane	1.26	1569	1228

The contrasting views on flammability limits are described by Dixon-Lewis and Isles (1959). Although the limits are often treated as fundamental properties, they state that the limits obtained experimentally are essentially convection or quenching limits, depending on the conditions.

In their review of flammability limits B. Lewis and von Elbe (1961) emphasize that, despite the theoretical problems, the experimentally determined limits have proved to be reliable for practical purposes. They state that there is no solution to the theoretical problem of flammability limits in terms of adiabatic one-dimensional propagation. Spalding's model represents the only feasible approach in terms of one-dimensional propagation, but the attribution of heat loss to radiation is not regarded as satisfactory by experimentalists, who prefer to believe that heat absorption by the unburned gas is the important effect.

The effect of the direction of propagation is illustrated by Lewis and von Elbe by the data shown in Table 16.17. They refer to the work of Linnett and Simpson (1957), who draw attention to the role of convection. Evidently convection currents are generated which are capable of quenching the flame. Such convectional quenching implies that heat is transferred to the unburned gas.

Lewis and von Elbe suggest that the mechanism of such quenching may be flame stretching. Stretching leads to extinction if the stretch exceeds a critical value of the Karlovitz number. The latter is inversely proportional to the burning velocity. Thus flames with low burning velocity, such as occur at the flammability limit, are particularly susceptible to stretch and hence extinction. These effects accord with the existence of narrow limits for downward propagation of the flame, since flame stretch is greater for downward propagation.

They also discuss the susceptibility of the flammability limits to diffusional stratification. Experiments by Coward and Brinsley (1914) in hydrogen–air mixtures with 4.1–10% hydrogen show that some hydrogen remains unburned. This effect has been explained by Goldmann and co-workers (Goldmann, 1929) as being due to diffusional stratification. Such stratification leads to local differences in concentrations and to locally increased burning velocities.

Lewis and von Elbe also mention that, according to the work of Markstein, upward flame propagation tends to promote cell formation. Cell formation, and Markstein's theory, are discussed below.

A further discussion of preferential diffusion is given by Furno *et al.* (1971). Coward and Jones (1952 BM Bull. 503) describe work on hydrogen–air mixtures in which burning is propagated upward by the buoyancy of individual flamelets and explain this by preferential diffusion. When the deficient reactant, in this case hydrogen, is the faster diffusing one, a flame zone concave to the burned gas will be enriched in this reactant. In downward propagation flame surfaces of small curvature are opposed by buoyancy, and the lean limit concentration is thus higher.

Furno *et al.* refer to the quantitative treatment of preferential diffusion given by Spalding (1955). He observed that the concentrations most easily ignited by electrostatic spark ignition were 0.9 and 1.8 stoichiometric ratios for methanol–air and heptane–air mixtures, respectively, and that the ratio of these two figures is close to the ratio $(D_o/D_f)^{\frac{1}{2}}$, where D_f and D_o are the diffusivities of the fuel and oxygen, respectively. Spalding suggests that the actual fuel–oxygen ratio in the developing flame kernel is stoichiometric. Furno *et al.* extend this argument and suggest that the ratio of the limits for upward and downward propagation may be given by this group also. They state that the data available to verify this hypothesis are sparse, but quote the results shown in Table 16.18.

Furno *et al.* also discuss the limit temperatures. It would be helpful if the rich limit temperature could be taken to be the same as the lean limit temperature. This would be equivalent to saying that in heavy hydrocarbon–air mixtures downward propagation reaches its limit at a stoichiometric ratio of about 1.9.

Several reviews of flammability limits have been given by Lovachev and co-workers (Lovachev, 1971, 1979; Lovachev *et al.*, 1973). Like earlier reviewers, Lovachev (1971) states that a theory based on radiant heat loss

Table 16.17 *Flammability limits: the effect of the direction of flame propagation (B. Lewis and von Elbe, 1987; after A.G. White, 1922, 1924) (Courtesy of Academic Press)*

Mixture	*Direction of propagation*	*Fuel concentration %*		*Stoichiometric fraction ratio*	
		Lower	Upper	Lower	Upper
Methane–air	Upwards	5.35	14.85	0.54	1.7
	Horizontal	5.40	13.95	0.54	1.6
	Downwards	5.95	13.35	0.60	1.5
Ethane–air	Upwards	3.12	14.95	0.54	2.9
	Horizontal	3.15	12.85	0.54	2.5
	Downwards	3.26	10.15	0.56	1.9
Pentane–air	Upwards	1.42	8.0	0.55	3.3
	Horizontal	1.44	7.45	0.56	3.1
	Downwards	1.48	4.64	0.57	1.9
Benzene–air	Upwards	1.45	7.45	0.53	2.9
	Horizontal	1.46	6.65	0.53	2.6
	Downwards	1.48	5.55	0.54	2.1

Table 16.18 *Stoichiometric ratios[a] of most easily ignited mixtures and of limit mixtures in upward and downwards propagation (after Furno et al. 1971) (Courtesy of the Combustion Institute)*

Mixture	$(D_o/D_f)^{\frac{1}{2}}$[b]	*Optimum ratio for ignition*	*Ratio of upwards to downwards propagation limit*
			Upper limit
Methane–air	0.96	0.9	1.02
Ethane–air	1.29	1.2	1.24
Propane–air	1.44	1.3	1.43
Butane–air	1.55	1.5	1.41
Pentane–air	1.63	–	1.72
Hexane–air	1.70	1.7	–
Heptane–air	1.78	1.8	–
Benzene–air	1.52	–	1.46
			Lower limit
Hydrogen–air	0.54	–	0.46
Methane–air	0.96	0.9	0.92

[a] Fuel concentration/stoichiometric fuel concentration.
[b] D_f, diffusivity of fuel; D_o, diffusivity of oxygen.

does not account for the experimental phenomena and prefers to explain flame extinction as due to heat loss into the unburned gas due to convection flows.

Lovachev *et al.* (1973) emphasize the role of convection. They state that agreement exists that convection is the reason for the difference between upward and downward propagation, but not on the mechanisms involved. They refer to three proposed mechanisms: Drozdov and Zeldovich (1943) have suggested unequal flame speeds and heat transfer; Linnett and Simpson (1957) have suggested differences in the flame surface; and B. Lewis and von Elbe (1961) have suggested flame stretching.

They quote a relation, derived by Lovachev (1971), for the flame velocity at the flammability limit. They discuss the question of whether the upward or downward propagation limit is more appropriately regarded as the true flammability limit. They acknowledge the practical reasons why Coward and Jones adopted the upward propagation limit, but opt for the downward propagation limit as the more fundamental.

They state that for hydrocarbon–air mixtures the lean limit flame temperature is approximately constant. Different experimental methods give different values, those obtained by the flat flame method being the lowest quoted. They draw attention to the results of Gibbs and Calcote (1959), who found that for such mixtures the flame speeds are similar. This suggests that the heat release and the flame temperature should also be similar.

Lovachev (1979) outlines the various factors which influence the measured flammability limits, which he terms the ignition scheme. He states that the flammability limits determined in a large chamber of volume $8\,m^3$ are wider than those given by the standard tube method. Thus there are some compounds which are classed as flammable by the former method, but which would be classed as non-flammable by tests conducted in the latter one. He describes experiments showing the buoyant deformation of the flame kernel in large confinements. The illustrations given show a transition from a sphere to a vertically oblated sphere with an inflection at its based, somewhat kidney-shaped.

Lovachev also describes the effect of turbulence on flammability limits and quotes several pieces of work which illustrate this. These include work by K.N. Palmer and Tonkin (1961) on propane–air mixtures in horizontal tubes. At flow velocities of 0.5 m/s the limits widened, but with a four-fold increase they narrowed again. He states that the experimental studies carried out on turbulence effects have been done with tubes that are too narrow and ignition sources that are too weak. He points out that flammability limits given in handbooks are for non-turbulent conditions, but that in practice turbulence effects are not negligible.

Macek (1979) discusses the concept that extinction occurs when the burning velocity is so low that it is overcome by the dissipation processes and refers to the accounts of these processes by Burgess (1969) and Burgess and Hertzberg (1975).

The effect of pressure on flammability limits is discussed by Egerton (1953), B. Lewis and von Elbe (1961) and Lovachev *et al.* (1973).

The temperature effect on flammability limits is discussed by Egerton (1953) and Lovachev *et al.* (1973).

Other aspects of flammability limits include the effect of additives and of inhibitors. Additives are discussed by B. Lewis and von Elbe (1961), and inhibitors are considered by Lovachev *et al.* (1973) and Lovachev (1979).

Further aspects of flammability limits are considered in Sections 16.3.10 on burning velocity and 16.3.11 on quenching.

16.3.9 Ignition phenomena

Ignition of a flammable mixture be effected either by raising the temperature of the bulk gas until it ignites spontaneously or by local ignition of a part of the gas. The modes of ignition considered here are principally:

(1) auto-ignition;
(2) local ignition –
  (a) spark ignition,
  (b) hot surface ignition,
  (c) friction and impact ignition,
  (d) hot gas jet ignition,
  (e) hot particle ignition,
  (f) flame torch and jet ignition,
  (g) compression ignition.

Auto-ignition

Auto-ignition, or spontaneous ignition, is of practical interest not only in relation to hazards, but also in combustion systems such as gas engines and turbines. Auto-ignition, though simple in concept, needs careful definition. A definition of such ignition has been given by Sage and Weinberg (1959), who state that if the temperature of an infinite volume of reactants at constant pressure is raised instantaneously and homogeneously above some critical value and maintained there, an explosion will occur homogeneously throughout the volume, thus forestalling flame propagation.

As these authors point out, available auto-ignition temperature (AIT) data are based on experiments far removed from the conditions of this definition. Under the conditions described ignition can occur even if the concentration of the gas mixture is outside the normal flammability limits. These limits constrain flame propagation, but in this case the ignition occurs homogeneously throughout the mixture and propagation is not involved.

Measurement of the AIT is usually carried out by heating the flammable gas mixture in a spherical vessel. With this method there is found to be an effect of the surface/volume ratio, the AIT decreasing as the vessel volume increases. This effect was observed by Setchkin (1954) and has been found by other workers.

A method of measurement which matches more closely their definition of the AIT has been described by Sage and Weinberg (1959). The method is a two-stage one. A series of experiments is conducted in which, in the first stage, the flammable gas mixture is brought to a temperature somewhat below the ignition temperature and, in the second stage, a small quantity of energy is added which ignites the gas. The AIT is found by extrapolation of these results to determine that temperature for which no additional energy is required.

The application of thermal theory to spontaneous ignition has been discussed by several workers, including P. Gray and Harper (1959a,b), Kuchta, Barkowiak and Zabetakis (1965) and Cullis and Foster (1973). For a spherical vessel with ignition at the centre the relation between the vessel radius r and the absolute ignition temperature T is, to a first approximation,

$$\ln r \propto 1/T \qquad [16.3.26]$$

It has been shown for a large number of fuels that if the AIT is plotted against vessel volume the lines pass through a single point, as shown in Figure 16.19 (Coffee (1982b), based on work by Beerbouwer (1974)).

A comparison of the values of the ignition temperature obtained in work using heated vessels (auto-ignition), hot wires and hot gas jets has been made by Kuchta, Cato and Zabetakis (1964). Their results are shown in Table 16.19. The values of the ignition temperature obtained with the Pyrex Erlenmeyer flask are appreciably lower than the other values.

The variation of ignition temperature with heat source dimensions has been discussed by Kuchta, Bartkowiak and Zabetakis (1965). They state that thermal theory predicts that the ignition temperature varies inversely with the logarithm of the heat source size, as in relation 16.3.26. While this behaviour was observed for one material studied (engine oil) over the whole range of surface areas, the other hydrocarbons tested exhibited in large vessels an ignition temperature appreciably lower than that predicted by this equation.

The variability of values of the AIT given in the literature has already been mentioned. This is illustrated by the values for methane quoted by C. Robinson and Smith (1984), which range from 537°C to 748°C. They state that the convention is to quote the lowest value found in the literature, but in the case of methane they could not determine the origin of the widely quoted value of 537°C and give the value of 601°C determined by themselves as the lowest of those for which experimental details are available.

The AIT of mixtures has been studied by Cullis and Foster (1974). They found that for the binary mixture studied (*n*-decane and 2,2,5–trimethylhexane) the ignition tendency is controlled largely by the more ignitable component. It was necessary to go to nearly 50% of the less ignitable component before the ignition temperature started to rise appreciably.

Ignition delay time

In spontaneous ignition there is an induction period, or ignition delay, before ignition occurs. This delay is of interest both theoretically in relation to reaction kinetics and practically in relation to ignition in combustion systems. The ignition delay may be as little as a fraction of a second at higher temperatures, or several minutes close to the AIT.

Ignition delay decreases with increasing temperature. Semenov (1959) has given the following relation:

$$\ln \tau = \frac{k_1 E}{T} + k_2 \qquad [16.3.27]$$

where E is the apparent activation energy, τ is the time delay and k_1 and k_2 are constants.

Ignition delay has been studied by many other workers, including Brokaw and Jackson (1955), Ashmore and Levitt (1959), P. Gray and Harper (1959a,b), Voevodsky (1959) and Bascombe (1967). For propane–air mixtures with flowing gas, Brokaw and Jackson found the following variations of ignition delay with oxygen concentration and pressure p:

$$\frac{1}{\tau} \propto [O_2]^{\frac{1}{4}} \qquad [16.3.28]$$

$$\propto \ln p \qquad [16.3.29]$$

but did not find a constant activation energy relation with temperature.

Spark ignition

Turning to local ignition, it is convenient first to consider spark ignition. Here the ignition energy is determined by using the spark between two electrodes to ignite the flammable gas mixture. Apart from its implications for hazards, spark ignition has long been of practical interest in for combustion in car engines and jet engines. A more recent aspect is lean burn engines for cars.

The results obtained for spark ignition energy are critically dependent on the electrode and spark arrangements. In early work this was not fully appreciated. In particular, the electrodes were usually too close together so that quenching occurred and the results obtained were too high.

It was suggested in early work, such as that of B.W. Bradford and Finch (1937), that there was a specifically electrical effect involving excitation of reactant molecules, but this suggestion was rejected by von Elbe (1953) in favour of a thermal effect.

A model of spark ignition has been developed by von Elbe and Lewis (1949) and von Elbe (1953) and is described by B. Lewis and von Elbe (1961). In simple terms, the argument is that the volume heated needs to exceed a certain critical size, otherwise the temperature gradient is too great and heat is lost too fast for combustion to be sustained. There is a minimum

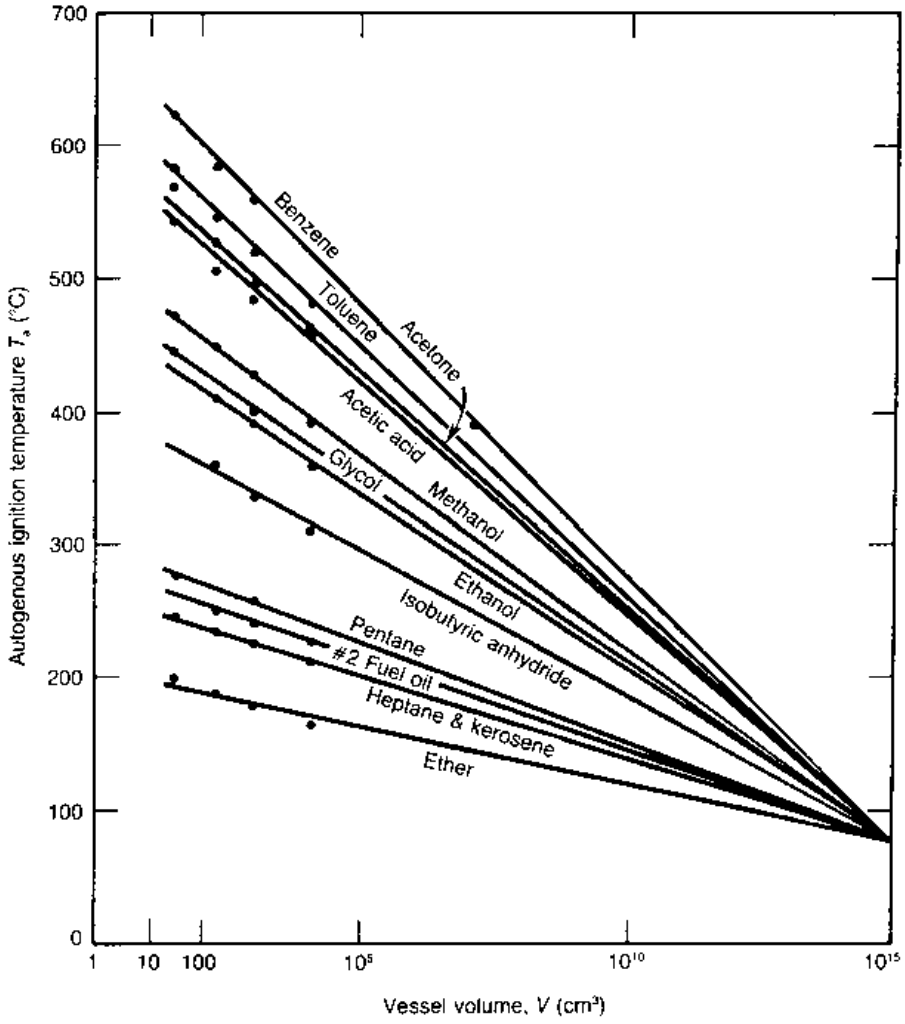


Figure 16.19 *Effect of vessel volume on the auto-ignition temperature (Reproduced with permission from Safety and Accident Prevention in Chemical Operations, 2nd ed., by H.H. Fawcett and W.S. Wood, Copyright ©, 1982, John Wiley and Sons Inc.)*

ignition energy needed to overcome quenching by the unburnt gas.

More formally, the theory envisages a preheat zone and a reaction zone. A heat balance is taken between a plane x in the combustion wave and the plane b where combustion is complete and, assuming that the heat transferred by mass diffusion is less than that transferred by heat conduction, the enthalpy per unit mass within the wave is larger than that at the boundary b of the burnt gas or that at the boundary u of the unburnt gas, the two latter being equal. Thus there is a wave of thermal energy, or excess enthalpy, travelling with the combustion wave. It is this excess enthalpy which ensures that the temperature gradient is such the heat flow into the preheat zone balances the heat liberated in the reaction zone. When a flame grows spherically, the combustion wave requires from some external source a continuous supply of excess enthalpy in proportion to the growth of its surface, until the wave has effectively become a planar one. On this theory the minimum ignition energy is equal to the excess enthalpy requirement of the minimum flame.

Von Elbe defines the minimum ignition energy H in terms of the excess enthalpy per unit area h and the critical diameter d at which the flame can propagate unaided:

$$H = \pi d^2 h \qquad [16.3.30]$$

There are a number of models of spark ignition, including those of Fenn (1951), Khitrin and Goldenburg (1957), Mayer (1957), Swett (1957), Penner and Mullins

Table 16.19 *Ignition temperatures of flammable gas mixtures with different heated surface areas (Kuchta, Cato and Zabetakis, 1964) (Courtesy of Combustion and Flame)*

Substance	*Ignition temperature* (°C)			
	Pyrex Erlenmeyer flask[a] *(2.2 cm radius, 13 cm long)*	*Cylindrical Pyrex vessel (0.5 cm radius, 15 cm long)*	*Inconel wire (0.5 cm radius, 5 cm long)*	*Air jet*[b] *(0.5 cm radius, >10 cm long)*
Methane	537	745	–	1040[c]
Ethane	515	580	–	840[c]
n-Butane	405	630	–	910[c]
n-Hexane	234	605	670	765
n-Octane	220	585	660	755
n-Decane	208	585	650	750
Benzene	562	685	–	1020[d]
Hydrogen	554	635	–	640[c]

[a] Minimum AIT values obtained in a 200 cm^3 Erlenmeyer flask equivalent cylinder radius 2.2 cm.
[b] Hot air jet injected into fuel–air mixture, except as noted by footnotes (c) and (d).
[c] Hot air jet injected into fuel only.
[d] Hot nitrogen jet injected into fuel–air mixture.

(1959), Rose and Priede (1959a,b), Ballal and Lefebvre (1975a), Adelman (1981), Maly (1981) and Sher and Refael (1982). A review of spark ignition models is given by Adelman.

Fenn (1951) derives the critical diameter of the spark kernel by equating the heat released in the volume of the kernel to that transferred across its surface. The minimum ignition energy H is then

$$H = \frac{K\pi d^3 c_p \rho}{6}(T_f - T_o) \qquad [16.3.31]$$

where T_f is the absolute adiabatic flame temperature and K is a constant. He states that the value of K is probably less than unity.

The model of Khitrin and Goldenberg (1957) is based on the thermal theory. Swett (1957) used long duration discharges and his treatment assumes that only part of this energy contributes to the ignition.

Ballal and Lefebvre (1975a) consider a spark kernel of the shape shown in Figure 16.20. It is assumed in this model that the heat release occurs only within the flame front, rather than throughout the whole kernel volume. The criterion for ignition is that the width d_c of the kernel is just equal to twice the width δ_L (laminar) or δ_T (turbulent regime) of the flame zone:

$$d_c = 2\delta_L \qquad \text{Laminar regime} \qquad [16.3.32a]$$

$$= 2\delta_T \qquad \text{Turbulent regime} \qquad [16.3.32b]$$

The authors give correlations for d_c for stagnant gas conditions and for laminar and turbulent flow regimes. For the stagnant gas condition

$$d_c = \frac{2k}{c_p \rho S_L} \qquad [16.3.33]$$

where S_L is the laminar burning velocity.

The model given by Adelman (1981) takes account not only of the heat balance on the spark kernel but also of the rate of growth of the kernel. Adelman states that spark kernels with the same spark energy input show identical growth in inert and combustible mixtures up to the critical point and that it is the spark discharge itself rather than combustion which is responsible for kernel growth up to this point.

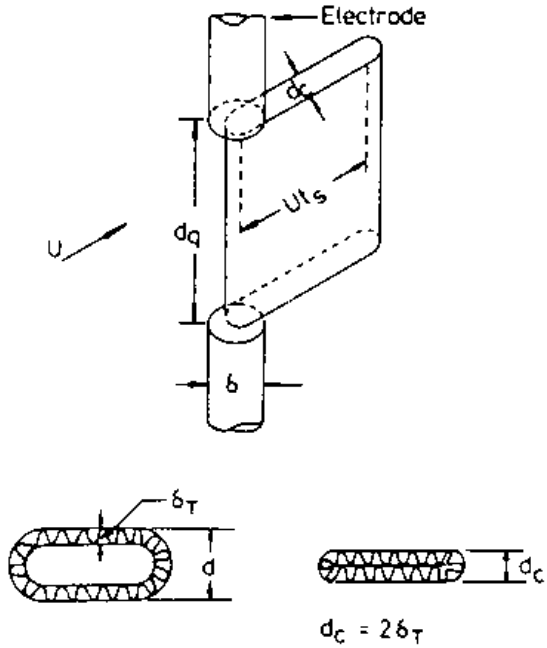


Figure 16.20 *Idealized model for the formation of a spark kernel (Ballal and Lefebvre, 1975a). d_q, quenching distance; t_s, spark duration; U, flow velocity (Courtesy of the Combustion Institute)*

In his review Adelman relates the critical diameter of the spark kernel to the flame thickness δ_L and gives

$$\delta_L \approx \frac{k}{c\rho S_L} \qquad [16.3.34a]$$

$$= \frac{\alpha}{S_L} \qquad [16.3.34b]$$

where $\alpha(=k/c_p\rho)$ is the thermal diffusivity. He defines a characteristic flame dimension l_L as the value of the group α/S_L at ambient conditions and states that the flame thickness is about $10l_L$. Critical radii tend to be of the order $5l_L$–$8l_L$ and thus about 0.5–0.8 of the flame thickness.

Maly (1981) distinguishes three modes of spark discharge – breakdown, arc and glow – and gives an ignition model. He emphasizes the importance of the breakdown mode. He states that ignition depends not so much on the total energy supplied but rather on high energy density deposition over a short time.

Minimum ignition energy

Work on measurement of ignition energy for spark ignition includes that of Blanc, Guest, von Elbe and Lewis (1947, 1949) and Moorhouse, Williams and Maddison (1974). The former determined ignition energies of hydrocarbon–oxygen–nitrogen mixtures over a range of concentrations, while the latter determined minimum ignition energies.

The problems in making such measurements have been discussed by a number of investigators. Rose and Priede (1959a) state that minimum ignition energies (MIEs) obtained by Lewis and von Elbe are some 1/100 of those obtained in early work in which the electrodes were too close together so that quenching could occur. Moorhouse, Williams and Maddison (1974) state that to obtain reproducible results they found it necessary to recondition the electrodes after about 15 trials.

The effect on the MIE of molecular structure is discussed by Moorhouse, Williams and Maddison.

The effect of turbulence on the MIE has been investigated by de Soete (1971). He states that turbulence causes an increase in the MIE, due mainly to an increase in flame front thickness, but also to a decrease in the fraction of energy which is effective.

Another study of the effect of turbulence is that of Ballal and Lefebvre (1975a). They state that the overriding effect of turbulence is heat loss by diffusion. They found that the MIE increases with increase in velocity and in turbulence intensity.

The effect of pressure and temperature on the MIE E is correlated by Moorhouse, Williams and Maddison (1974) as follows:

$$E = AP^{\alpha}T^{\beta} \qquad [16.3.35]$$

where P is the absolute pressure, T is the absolute temperature, A is a constant and α and β are indices. The values of the indices α and β were approximately 2 and -2, respectively.

Measurements of hot wire ignition energies have been made by number of workers, including Stout and Jones (1949). Different combinations of excitation current and time were used and the ignition energy was found to increase as the current was decreased and the time increased. A linear relation between the MIE and excitation time t was found:

$$E = A + Bt \qquad [16.3.36]$$

Hot surface ignition

Another mode of local ignition is contact with a hot surface. The AIT sets a lower limit to the temperature at which a hot surface may cause ignition, but it has long been known that in most situations of practical interest the hot surface temperature required to cause ignition is considerably higher than the AIT.

Interest has therefore centred on the difference between the hot surface ignition temperature and the AIT, or temperature excess. Research has shown that this temperature excess is a function of the material, area and geometry of the hot surface, of the gas and gas concentration, and the fluid flow and heat transfer conditions.

Some gases which have been widely used in work on hot surface ignition include methane, propane, butane and pentane. The AITs of these gases are 595, 470, 360 and 285°C, respectively.

Guest (1930 BM Tech. Pap. 475) investigated the ignition temperature of methane–air mixtures using various hot surface materials and areas up to 108 mm^2, and obtained values of 897–1420°C.

The effect of the area of the hot surface has been studied by Rae, Singh and Danson (1964), who exposed a methane–air mixture to hot surfaces of different size. Some typical results are shown in Figure 16.21. The work on hot particles by Silver (1937) and Paterson (1939–), described below, shows a similar decrease of the temperature excess as the hot surface area increases.

The effect of gas velocity has been studied by Mullen, Fenn and Irby (1949), who were concerned with the ignition of gas flowing past heated rods at high velocity as in a jet engine. Working with pentane–air mixtures, they found that the temperature excess increased with gas velocity.

Gas velocity has also been investigated by Goodall and Ingle (1967), who studied the ignition of kerosene in a wind tunnel. The hot surface temperature required to cause ignition in the experiments was as follows:

Gas velocity (m/s)	*Surface temperature for ignition* (°C)
0.3	405
1.5	660
3.0	775

The AIT of kerosene is given as 208–257°C, depending on the method of measurement

A number of workers have studied ignition of a flammable gas–air mixture on a vertical plate. A criterion widely used in this work has been the van't Hoff criterion that ignition occurs when the temperature gradient normal to the hot surface at some point becomes zero. Investigations have been done under forced convection by Toong (1957) and under natural convection by Ono *et al.* (1976).

L.D. Chen and Faeth (1981a) found that the zero temperature gradient condition is not always the appropriate one, that the plume above the hot surface influences ignition and needs to be taken into account, and that near limiting conditions there needs to be a substantial distance above the surface for the deflagration

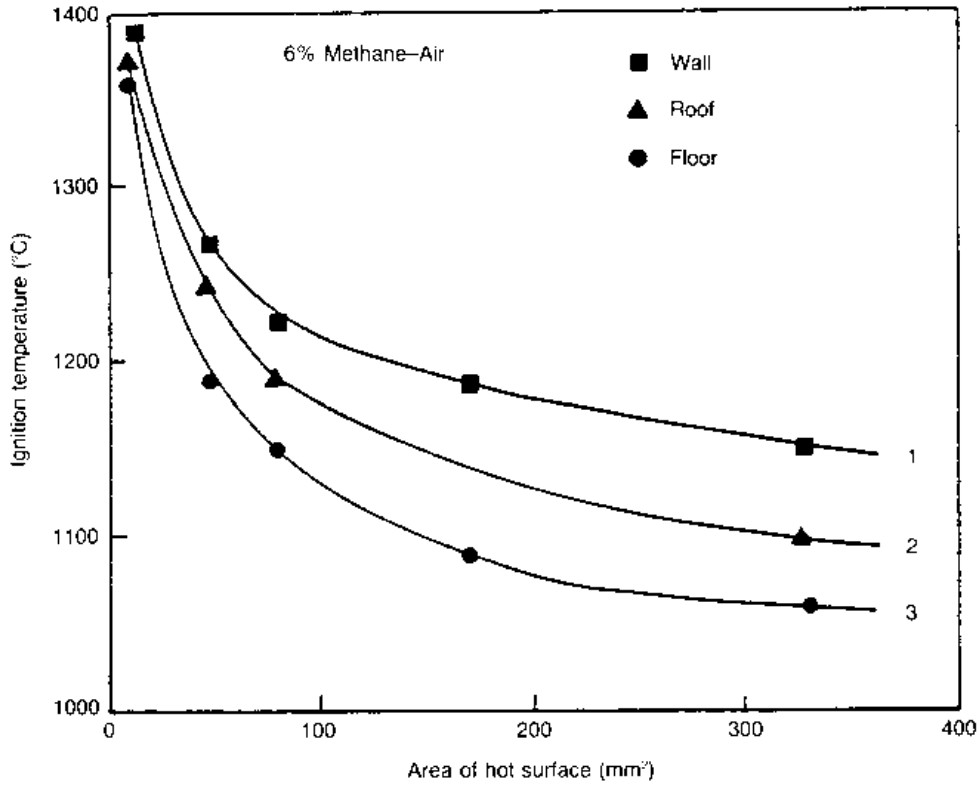


Figure 16.21 *Hot surface ignition temperature: effect of hot surface area on ignition temperature (Laurendeau, 1982; after Rae, Singh and Danson, 1964) (Courtesy of Combustion and Flame)*

wave to develop so that quenching surfaces may suppress the deflagration.

Sharma and Sirignano (1969, 1970) have studied other geometries. An extensive investigation of the parameters influencing hot surface ignition has been conducted by Bull and co-workers.

Hot surface ignition is essentially a two-stage process, with initiation of a cool flame in the first stage followed by 'hot' ignition. A distinction is made between ignition and propagation. Propagation is confined between the flammability limits, but auto-ignition is not so bounded. In constant volume tests substantial, rapid pressure rises have been obtained with very rich mixtures.

Bull has conducted experiments using a parallel plate reactor (D.C. Bull and Quinn, 1975; D.C. Bull, 1977). In this apparatus the hot surface is placed above a cold surface so as to limit heat transfer to the conduction mode. Studies were conducted on propane, butane and hexane, and ignition diagrams for these gases obtained. The absolute results depended on the design of the apparatus, but certain trends emerged. A typical ignition diagram is shown in Figure 16.22. The figure shows the effect of the surface temperature. Another result of this work is to demonstrate that if there is even a modest temperature gradient normal to the hot surface, a much higher temperature excess is required for ignition.

D.C. Bull, Cairnie *et al.* (1980) have also described research directed at understanding of the influence of fluid flow on hot surface ignition. Experiments were done on ignition by a hot vertical plate under laminar flow conditions. These conditions are favourable for experimentation and modelling and also approximate to the practical cases of a hot vertical surface or a hot large diameter pipe. The work showed that as the gas flows over the vertical surface it undergoes self-heating. Figure 16.23 gives the results obtained for a non-reacting gas and for a reacting gas.

The authors found that their initial model with reaction kinetics based on the Arrhenius equation was deficient. It predicted thermal runaway when the van't Hoff criterion of zero temperature gradient is satisfied, but this did not fit the experimental results. A second, more complex model, based on the acetaldehyde kinetics model, described below, was more successful. Figure 16.24 shows some predictions given by this latter model.

Bull and Grant (D.C. Bull and Grant, 1975; D.C. Bull, 1977) have investigated ignition by a hot horizontal pipe, using two concentric pipes. They found that there was a region of high temperature gradient at the hot inner pipe, then a region of nearly constant temperature, then a cool region at the cold outer pipe. Ignition occurred in the region of nearly constant temperature. They derived

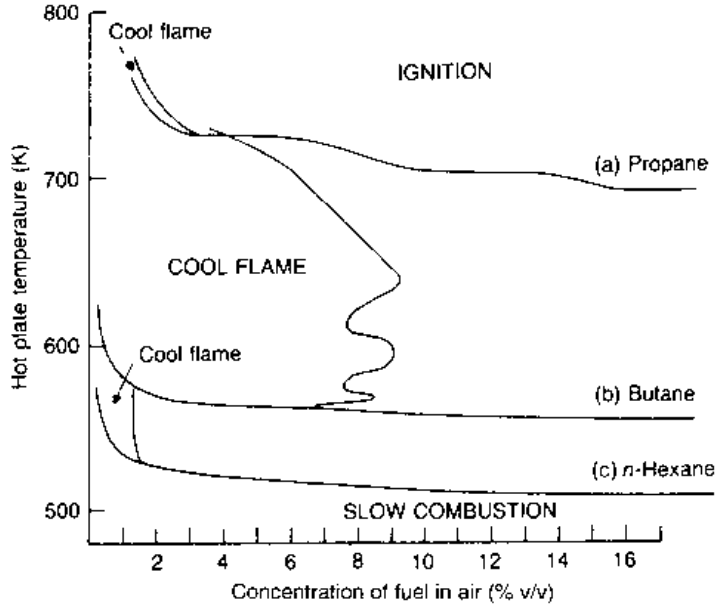


Figure 16.22 *Hot surface ignition temperature: ignition temperature boundaries for selected fuel–air mixtures in a parallel plate reactor (D.C. Bull, 1977). Plate separation 50 mm; `hot' and `cold' plates at the same temperature – see text (Courtesy of DECHEMA)*

a model, correlating their results in terms of the ratio of the pipe diameters, the Rayleigh number and the temperature across the annular gap.

Work was also done to investigate ignition by a hot exhaust pipe in the open air. The model showed that for ignition to occur there would need to be a very high temperature excess with high convective flows and ignition in the wake of the pipe. Under these conditions the residence time in the hot region may be less than the induction time.

Work on the development of a model for hot surface ignition has been described by Harrison and Cairnie and co-workers (A.J. Harrison and Cairnie, 1988; A.J. Harrison *et al.*, 1988). These authors have developed a chemical reaction model for the hot surface ignition of acetaldehyde–air mixtures. The full model is a 20-reaction model, but has been simplified successively to 8-, 5- and 2-species models. Some success has been achieved in describing the initiation of cool flame behaviour for hot vertical plate and continuous stirred tank reactor configurations. Below about 500°C, the ignition process depends critically on a build up of intermediate compounds. This indicates that the one-step ignition model often used is inappropriate.

Bartknecht (1988) has described work on ignition by steel pins heated by rubbing against a steel wheel. The pins were 6 and 8 mm in diameter with heated surfaces of area 2.9 and 4.0 cm^2, respectively. The lowest temperatures which he reports for ignition are 1248°C for methane and propane, and 1169°C for butane.

Work on ignition by heated rods has been described by Adomeit (1965), who investigated, in particular, ignition delay.

Friction and impact ignition

If one body strikes another, ignition may occur by impact or friction. In either case the ignition occurs as a result of a rise in surface temperature. If one body strikes another normal to its surface, there is impact but little friction. Impact causes a surface temperature rise in two ways (Bowden and Tabor, 1954). Kinetic energy is converted to heat. This causes a surface temperature rise which may lead to exothermic oxidation of the surface resulting in a further temperature rise. The second of these effects tends to predominate.

The surface temperature rise depends on the oxidation characteristics and the thermal conductivity and does not simply correlate with the energy of impact. The heat generated by oxidation is highest for easily oxidizable metals such as iron and aluminium. The heat of oxidation of iron is several times that of copper and its thermal conductivity is less; the surface temperature rise of iron exceeds that of copper.

If one body is pressed against the surface of another and made to move, there is friction and this causes a surface temperature rise. If the first body strikes the second at an angle, there is a combination of impact and friction, which is described as frictional impact.

It has long been known that incendive sparks may be produced by striking rusty steel covered with aluminium paint. The effect is due to a chemical reaction, known as the thermite reaction. In this reaction the temperature can reach 3000°C. Following a study in 1941 by the Safety in Mines Research Board, which showed that no sparks were obtained unless the steel surface was rusty and that the effect varied with the type of paint, work was done by Kingman, Coleman and Rogowski (1952) to

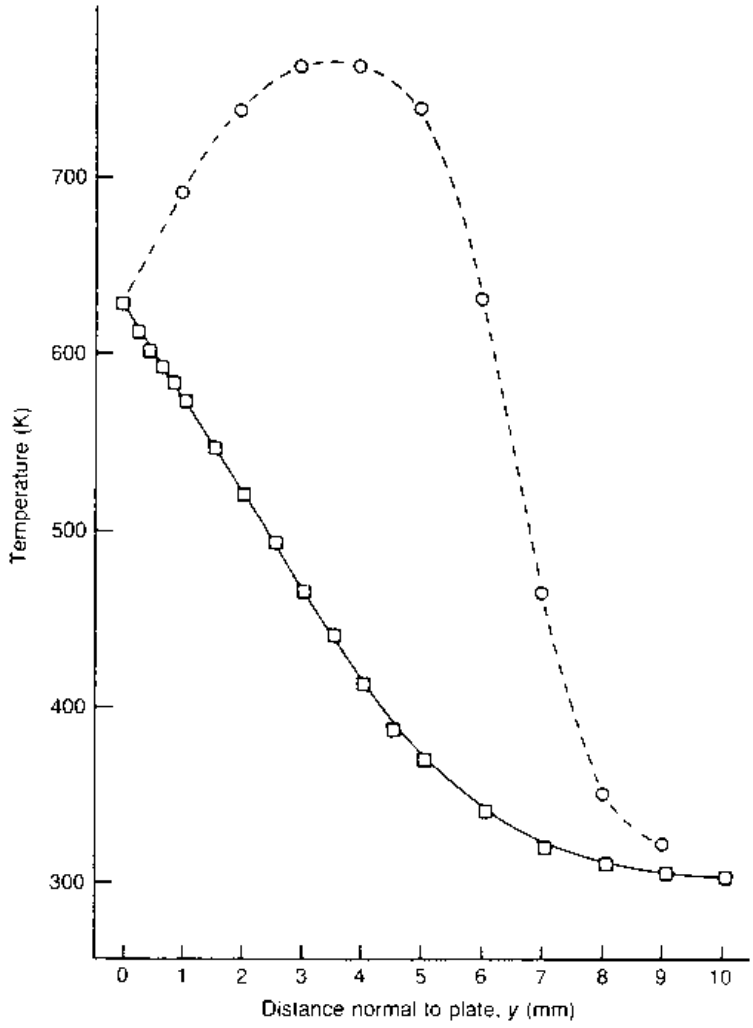


Figure 16.23 *Hot surface ignition temperature: boundary layer temperature profiles (D.C. Bull et al., 1980). (□) experimental values for air (non-reacting flow); (○) experimental values for 7.1% diethyl ether–air mixture (reacting flow); and (--) theoretical values for air. Plate temperature 623 K; distance up plate 0.1 m. Reproduced with permission*

define more closely the conditions under which this effect occurs. Using both ferrous and non-ferrous strikers, they confirmed that sparks occurred only if rust was present. They found that no oil bound paint gave sparks unless the specimen had been preheated to at least 150°C. Cellulose nitrate paints, however, gave sparks after preheating to 100°C. In an appended note, HM Senior Chemical Inspector of Factories stated that the earlier report had given rise to exaggerated fears and that aluminium paint could be used in hazardous areas provided cellulose nitrate based paints were avoided and that no aluminium paint, whatever its base, should be used if it was likely to be heated to 150°C.

A review of ignition by friction and impact has been given by F. Powell (1969), with particular reference to ignition of firedamp in coal mines. He states that frictional heating, usually by coal cutting machines, is the largest single cause of ignition in British mines. With regard to surface temperature rise he states that impact normal to the surface tends to give a relatively small surface temperature rise, that sliding friction gives surface temperatures sometimes approaching the melting points of the two materials and that frictional impact sometimes gives surface temperatures equal to the melting points. He reviews impact or rubbing between rocks, impact or sliding of metals on rocks, impact or

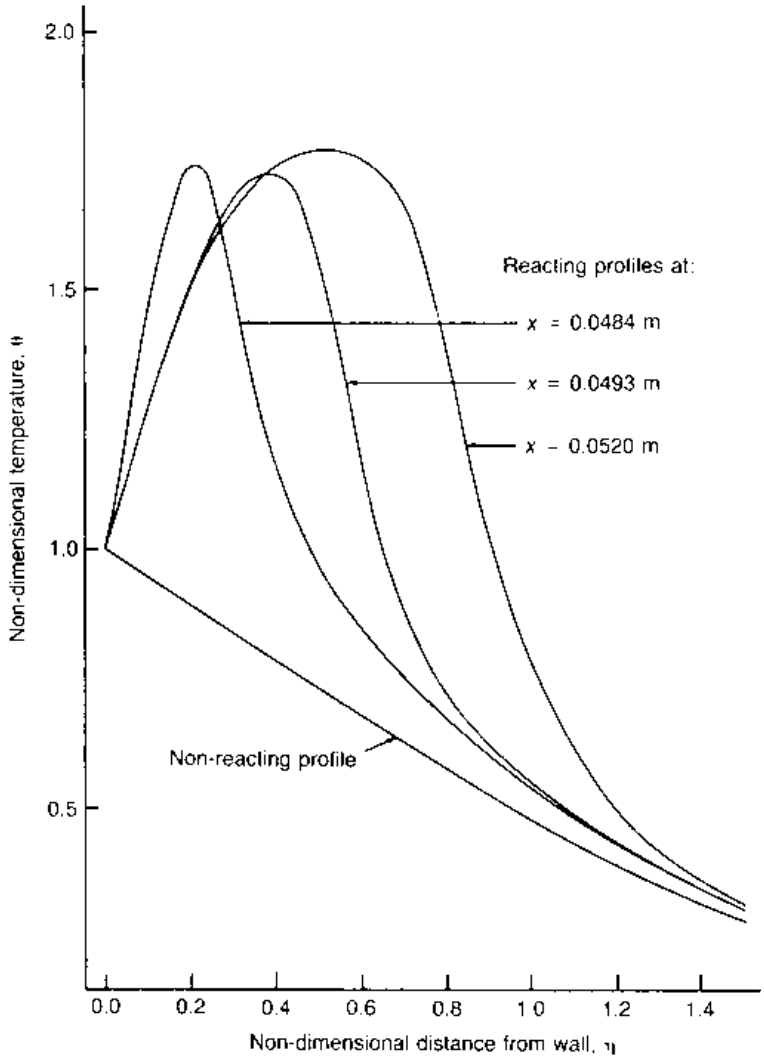


Figure 16.24 *Hot surface ignition temperature: theoretical boundary layer temperature profiles in a parallel plate reactor.* $\theta = (T - T_\infty)/\Delta T$; $\eta = [(g\Delta T^2\rho_\infty)/(4T_\infty\mu_\infty^2)]^{\frac{1}{4}}\frac{1}{x}\int^y \frac{\rho}{\rho_\infty}\,dy$ *(D.C. Bull et al., 1980). Reproduced with permission*

rubbing between metals, and grinding and drilling operations.

In a study of impact of metals on metals, Titman and Wynn (1954) ignited methane–air mixtures with steel balls shot at steel and aluminium targets. Burgess and Wheeler (1929) were able to ignite methane–air mixtures with a steel locomotive wheel rubbing on steel rails, but only by using a shield to concentrate the sparks.

Powell describes extensive work in which ignition of mainly methane–air mixtures has been obtained by the impact of light alloys such as aluminium. In most cases ignition was by the thermite reaction. It is characteristic of light alloys that they tend to give a smear on rusty steel. Even if ignition does not occur at the time, a glancing blow from a hard object at some later time may produce the thermite reaction and cause ignition. For this reason the use of light alloys in British mines is severely restricted. However, ignitions have been obtained with light alloys where neither rust nor steel were involved. W.G. Thomas (1962) ignited methane–air mixtures by shooting aluminium pellets at clean steel targets. In an investigation of an explosion in a ship's tank, Rae (1965) obtained ignitions of methane–air mixtures by dropping brass onto partly consumed magnesium anodes.

Ignition by the frictional impact of steel on rock has been studied by Blickensderfer (1975) in connection with ignition by coal-cutting machines. In severe impact a

smear of molten metal is deposited on the rock. Most of the impact energy is converted to heat at the interface. This hot smear has the potential to ignite methane–air mixtures. In experimental work in which a metal object representing a cutting tool was secured to a flywheel and made to impact on rock, it was found that the impact energy had little effect on the probability of ignition, but that the impact speed had a strong effect. Hot streak temperatures of 1400°C were obtained. The effect of an increase in the impact speed was to increase the area rather than the temperature of the hot surface. This work includes a model of hot smear ignition.

Ignition of methane–air mixtures has been obtained by both ferrous and non-ferrous metals striking against quartzitic materials, such as sandstone or concrete containing sand. This work is relevant to the use of 'non-sparking' tools.

Hot gas jet ignition

Ignition of flammable gas–air mixtures by jets of hot gas has been studied by Wolfhard and Vanpee (1959) to determine the degree of hazard of ignition of methane in coal mines from hot spent gases from the detonation of an explosive charge.

Ignition temperatures for a hot jet of air entering a cold, pure fuel are shown in Table 16.20 and those for a hot jet of nitrogen entering an ethylene–air mixture at an optimum concentration (close to stoichiometric) for ignition are shown in Table 16.21.

Table 16.20 *Hot gas jet ignition: ignition temperatures of a hot air jet entering a cold, pure fuel (Wolfhard and Vanpee, 1959) (Courtesy of the Combustion Institute)*

Fuel	*Ignition temperature* (°C)
Methane	1190
Ethane	945
Propane	1010
n-Butane	1025
Ethylene	875
Propylene	1060
iso-Butylene	1070
Acetylene	755
Carbon monoxide (commercial)	765
Hydrogen	670

Table 16.21 *Hot gas jet ignition: ignition temperatures for a hot jet of nitrogen entering an ethylene–air mixture of optimum concentration (close to stoichiometric) for ignition (Wolfhard and Vanpee, 1959) (Courtesy of the Combustion Institute)*

Jet flow (cm^3/s)	*Maximum temperature within jet* (°C)
25	1020
35	1035
50	1040
70	1050
100	1100
130	1140

Hot particle ignition

Investigations of the ignition of flammable gas–air mixtures by hot particles have been conducted by Silver (1937) and Paterson (1939–). Hot particles are another potential source of ignition in the use of blasting explosives in coal mines.

Silver carried out experiments in which hot particles were injected into flammable gas–air mixtures. The gases were coal gas, pentane and hydrogen and the particles quartz and platinum. The particle velocities were in the range 2–5 m/s. The particle temperature necessary to give ignition decreased as the particle diameter increased. Figure 16.25 shows some results obtained for the effect of particle diameter on the particle temperature required for ignition.

Paterson extended this work, using a wider range of gases and materials and particle velocities up to 65 m/s. Some results showing the effect of particle velocity and diameter on the particle temperature required for ignition are shown in Figure 16.26. Paterson's work shows that for small particles and for high particle velocities the surface temperatures required for ignition are very high.

A model for ignition by a hot inert particle has been described by Su, Homan and Sirignano (1979). Sharma and Sirignano (1970) have given a model for ignition by a hot projectile.

Flame torch and jet ignition

Flame torch ignition of a flowing flammable gas mixture is important in combustion systems. The work of Mullen, Fenn and Irby (1949) has already been mentioned. Work on this topic has also been done by Wang *et al.* (1981). Ignition of a vapour cloud by a flame jet has been studied by Mackay *et al.* (1988) in the context of vapour cloud explosions. These are described in Chapter 17.

Compression ignition

If a mixture of flammable gas and air is compressed, the resultant temperature rise may take the mixture into the temperature range in which auto-ignition occurs. This effect is exhibited in the diesel engine and is sometimes known as the diesel effect.

There is a considerable body of work on compression ignition, coming from several sources. Compression ignition is another of the modes of ignition studied in relation to ignition of firedamp in coal mines. Ignition by the pressure wave from a blasting explosive has been investigated by W.C.F. Shepherd (1949).

Another motivation for research on compression ignition is the study of fast chemical reactions. Compression is a convenient method of effecting the very rapid translation of a reaction mixture into the temperature range of interest. The technique has been described by Jost (1949). According to Jost, for hydrocarbon–air mixtures over the temperature range of interest the value of the ratio of specific heats γ is about 1.3. He also states that the variation with hydrocarbon concentration is not negligible.

A major aspect of research on combustion is the behaviour of shock waves, and ignition by shock waves is one aspect of this. Such work has been described by J.W. Meyer and Oppenheim (1971b), Vermeer, Meyer and Oppenheim (1972) and Eubank *et al.* (1981). Regimes of weak and strong ignition and ignition time

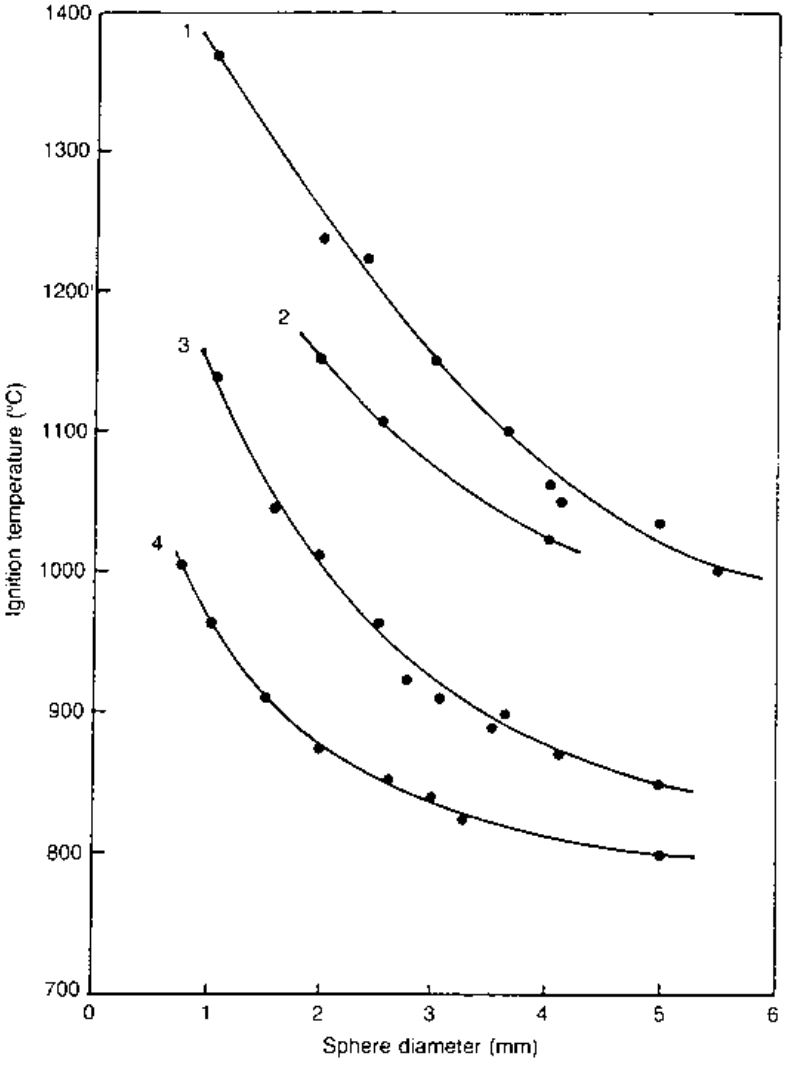


Figure 16.25 *Hot surface ignition temperature: effect of particle diameter on the particle temperature required for ignition of fuel–air mixtures by a hot particle travelling through the mixture (Laurendeau, 1982; after Silver, 1937; and Paterson, 1939–) 1, 3% pentane at ≈4 m/s; 2, 3% pentane at ≈1.2 m/s; 3, 10% coal gas at ≈4 m/s; 4, 10% coal gas at ≈1.2 m/s (Courtesy of Combustion and Flame)*

delay are features that have been particularly investigated.

Research into internal combustion engines and diesel engines is another source of work on compression ignition. Work on compression ignition, and 'knock', in internal combustion engines is illustrated by the work of Halstead *et al.* (1975). There are also some studies of compression ignition of particularly sensitive chemicals such as those by Beeley, Griffiths and Gray (1980) on isopropyl nitrate and J.F. Griffiths and Perche (1981) on ethylene oxide.

Ignition in compression is a form of auto-ignition. The comment made earlier is therefore applicable, that, given a homogeneous mixture, ignition may occur outside the normal flammability limits, since these apply essentially to propagation of the flame.

16.3.10 Burning velocity

It is usual to distinguish between flame speed, which is the actual speed of the flame front in a given situation, and burning velocity, which is a property, or at any rate a quasi-property, of the flammable gas mixture. Definition of the burning velocity is not, however, straightforward.

Linnett (1953) states that it seems impossible to define a burning velocity which is equally applicable to both planar and spherical flames and will have the same value for both cases, but suggests that the best approach is to use a value obtained by dividing a suitable flame area

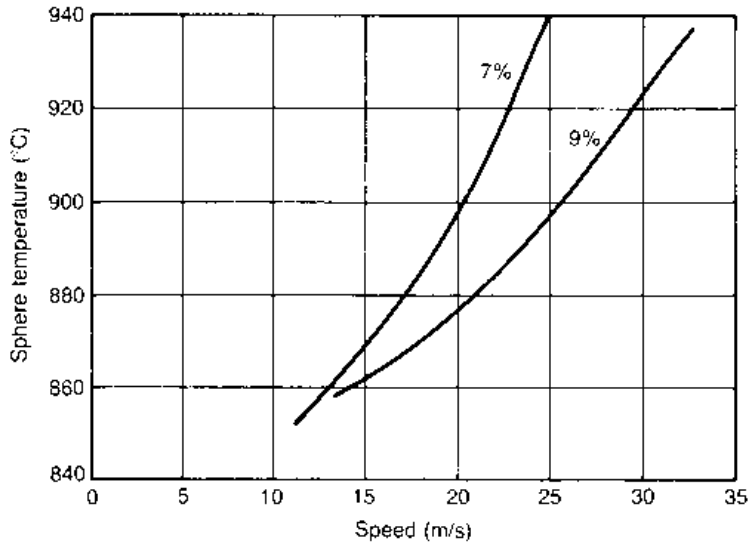


Figure 16.26 *Hot surface ignition temperature: the effect of particle velocity on particle temperature for the ignition of fuel–air mixtures by a hot particle travelling through the mixture (after Paterson, 1939–) Parameter of curves is concentration of coal gas in air (% v/v) (Courtesy of the Philosophical Magazine)*

into a volumetric flow rate. It has been shown by Spalding and Yumlu (1959) that there are in fact two burning velocities, the higher value normally being the stable one.

There are a number of methods available for the measurement of burning velocity. These are reviewed by Linnett (1953) and by Andrews and Bradley (1972b). They include:

(1) propagating flame methods –
  (a) soap bubble,
  (b) bomb,
  (c) tube,
  (d) flame kernel;
(2) cylindrical burner –
  (a) cone angle,
  (b) total area;
(3) nozzle burner –
  (a) cone angle,
  (b) total area.

With the cylindrical burner and nozzle burner methods measurement may be based on luminous flame, shadow or schlieren techniques.

A model for a spherical flame is given in Chapter 17. Other early models, including those by Semenov (1940), Tanford and Pease (1947) and Manson (1949), are reviewed by Dugger and Simon (1953). Further rather more complex models have been given by Yang (1961) and by Spalding, Stephenson and Taylor (1971).

Near the limits of flammability there is a minimum burning velocity to sustain combustion. This minimum burning velocity is influenced by natural convection. It has been suggested by Simmons and Wright (1972) that the following equation, derived by R.M. Davies and Taylor (1950) for the rise of an air bubble up a tube through a denser fluid, may be applied to the rise of a bubble of hot gas through a flammable gas mixture:

$$v_o = 0.464(gr)^{\frac{1}{2}} \qquad [16.3.37]$$

where g is the acceleration due to gravity (cm/s^2), r is the radius of the tube (cm) and v_o is the velocity of the bubble (cm/s).

The effects of pressure and temperature on burning velocity have been the subject of several studies including those by Andrews and Bradley (1972a, 1973a), Halstead, Pye and Quinn (1974), Gülder (1982) and Iijima and Takeno (1986).

For methane, Andrews and Bradley (1972a, 1973) found that the burning velocity decreases with increasing pressure according to the relation

$$S_u \propto P^{-m} \qquad [16.3.38]$$

where $m = 0.5$. A similar relation was obtained by Gülder (1982) for methanol, ethanol and *iso*-octane with values of m of the order of 0.2. On the other hand, for hydrogen, Iijima and Takeno (1986) report an increase in burning velocity with pressure.

Burning velocity is generally reported to increase with temperature. Gülder (1982) found the relation

$$S_u \propto T^n \qquad [16.3.39]$$

where $n = 1.75$ for methanol and ethanol and $n = 1.56$ for *iso*-octane. Andrews and Bradley (1972a) obtained for methane the relation

$$S_u = 10 + 0.000371T_u^2 \qquad [16.3.40]$$

where S_u is the burning velocity (cm/s) and T is the absolute temperature of the unburned gas. IIjima and

Takeno (1986) obtained similarly strongly positive correlations of burning velocity with temperature for both methane and hydrogen.

The effect of physical and chemical properties on burning velocity has been studied by Golovina and Fyodorov (1957). The effect on burning velocity of the recirculation of the products of combustion has been investigated by Putnam (1974).

The variability in the values of burning velocity given in the literature is discussed by Andrews and Bradley (1972b). For methane they quote values ranging from 31 to 50 cm/s and the variation is as great for most of the other gases considered.

Relations for the burning velocity of mixtures have been given by Payman and Wheeler (1922) and Spalding (1956). The Payman and Wheeler rule is

$$S_{u,m} = \Sigma S_{u,i} y_i \qquad [16.3.41]$$

where y is the mole fraction in the fuel–oxidant mixture and subscripts i and m denote component i and the mixture, respectively.

Spalding's treatment is based on the concept that the sole effect of mixing two fuel–air mixtures is to alter the flame temperature to a common value. In the simplified form given by Yumlu (1967a), the Spalding rule is

$$S_{u,m}^2 = \Sigma S_{u,i}^2 \alpha_i \qquad [16.3.42]$$

where α is the ratio of the mass of fuel i and the corresponding amount of oxidant to the total mass of fuel and oxidant.

The burning velocity so far considered is the laminar burning velocity S_L. The burning velocity is increased by turbulence and it is necessary to consider also the turbulent burning velocity S_T.

The definition of burning velocity becomes more difficult if the conditions are turbulent. The definition is usually given in terms of the flame surface, but this surface is difficult to specify. A rigorous definition of turbulent burning velocity has been given by J.M. Richardson (1956). Its application has been discussed by Palm-Leis and Strehlow (1969).

Measurement of the turbulent burning velocity has usually been carried out utilizing a modification of the burner method used for laminar burning velocity. The method of flame propagation in a vessel has also been used.

There are a number of correlations and models of turbulent burning velocity. Most of these involve parameters for the turbulence due to the gas flow such as the axial component of turbulence u' and the radial component v'. Turbulence generated by the flame is also taken into account in some treatments.

Treatments of turbulent burning velocity have been reviewed by B. Lewis and von Elbe (1961). The first model was that by Damköhler (1940), who suggested that the flame front is strongly distorted by turbulence and that under these conditions for a stable flame the burning velocity must exceed not only the average velocity U but also the velocity $U + u'$. This leads to the relation

$$S_T \propto u' \qquad [16.3.43]$$

In this model S_T is independent of S_L.

Shchelkin (1943) modified the Damköhler model by assuming that the distortions of the flame front are cone shaped. Then from geometrical considerations he obtains

$$\frac{S_T}{S_L} = [1 + (2u'/S_L)^2]^{\frac{1}{2}} \qquad [16.3.44]$$

The model is a crude one, and in recognition of this the 2 in Equation 16.3.44 may be replaced by an undetermined number B of the order of unity. Equation 16.3.44 reduces to relation 16.3.43 for large values of $(u'/S_L)^2$.

Thus, according to these theories, under conditions of high turbulence the turbulent burning velocity S_T should be independent of the fuel gas. Work by D.T. Williams and Bollinger (1949) has shown, however, that this is not so.

Karlovitz, Denniston and Wells (1951) have developed a model which addresses this problem. The model is based on the concept of an undulated flame front and yields the relations

$$\frac{S_T}{S_L} = 1 + \frac{S_t}{S_L} \qquad [16.3.45]$$

with

$$S_t = \left(2S_L u' \left\{1 - \frac{S_L}{u'}[1 - \exp(-u'/S_L)]\right\}\right)^{\frac{1}{2}} \qquad [16.3.46]$$

where S_t is the average velocity of displacement of the turbulent wave. At low turbulence, Equation 16.3.46 reduces to

$$\frac{S_T}{S_L} = 1 + \frac{u'}{S_L} \qquad 1 < \frac{u'}{S_L} \qquad [16.3.47]$$

and at high turbulence it reduces to

$$\frac{S_T}{S_L} = 1 + \left(\frac{2u'}{S_L}\right)^{\frac{1}{2}} \qquad \frac{u'}{S_L} > 1 \qquad [16.3.48]$$

In this model, therefore, the turbulent burning velocity remains dependent on the laminar burning velocity, even at high turbulence.

In their work, D.T. Williams and Bollinger (1949) obtained the correlation

$$u_t = 0.1761 u_n d^{0.2564} \mathrm{Re}^{0.238} \qquad 3000 < \mathrm{Re} < 35\,000 \qquad [16.3.49]$$

where d is the burner diameter (cm), u_n is the laminar burning velocity (cm/s) and u_t is the turbulent burning velocity (cm/s).

Fine (1958) describes two models for the effect of turbulence on burning velocity. One treatment is based on the effect of turbulence in inducing flame wrinkling and gives

$$\frac{S_T}{S_L} = f(u'/S_L) \qquad [16.3.50]$$

The other model involves the effect of turbulence on thickening of the reaction zone. Fine applied these models in an attempt to determine by studying the effect of pressure whether the Reynolds number is the proper correlator, but the results were inconclusive.

Correlations of the turbulent burning velocity have been given by a number of workers. Thus Kozachenko (1962) gives a relation of the form

$$S_T = S_L + \phi_1 \qquad [16.3.51]$$

and Gökalp (1980) one of the form

$$S_T = S_L + \phi_2 \qquad [16.3.52]$$

where ϕ_1 and ϕ_2 are functions of turbulence.

An extensive programme of work on the turbulent burning velocity has been undertaken by Bradley and co-workers. Andrews, Bradley and Lwakabamba (1975a) obtained a graphical correlation of turbulent burning velocity in terms of the unburnt gas Reynolds number defined as

$$R_\lambda = u'\lambda/\nu \qquad [16.3.53]$$

where u' is the root mean square (rms) turbulent velocity, λ is the Taylor microscale and ν is the kinematic viscosity. On the assumption that $u'/U = 0.05$ this Reynolds number is given approximately by the relation

$$R_\lambda = (\mathrm{Re} - 2500)^{\frac{1}{2}} \qquad [16.3.54]$$

Abdel-Gayed and Bradley (1977) present a further graphical correlation. For high turbulence they give the relation

$$\frac{u_t}{u_l} = 3.788 R_\lambda^{0.238} \qquad R_\lambda > 100;\ u_l/u' \to 0 \qquad [16.3.55]$$

where u_l and u_t are the laminar and turbulent burning velocities, respectively. Further work is reported by Abdel-Gayed and Bradley (1987), who also give details of the correlations found by previous workers.

Continuing this investigation, Bradley, Lau and Lawes (1992) give the correlation shown in Figure 16.27. They use an integral length scale of turbulence L such that

$$\frac{\lambda^2}{L} = \frac{A\nu}{u'} \qquad [16.3.56]$$

with a turbulent Reynolds number Re_L defined by

$$\mathrm{Re}_L = \frac{u'L}{\nu} \qquad [16.3.57]$$

where A is a constant. Then for the parameter group $K\mathrm{Le}$ in Figure 16.27 they give for the Karlovitz flame stretch factor K the relation

$$K = 0.157\left(\frac{u'}{u_l}\right)^2 \mathrm{Re}_L^{-\frac{1}{2}} \qquad [16.3.58]$$

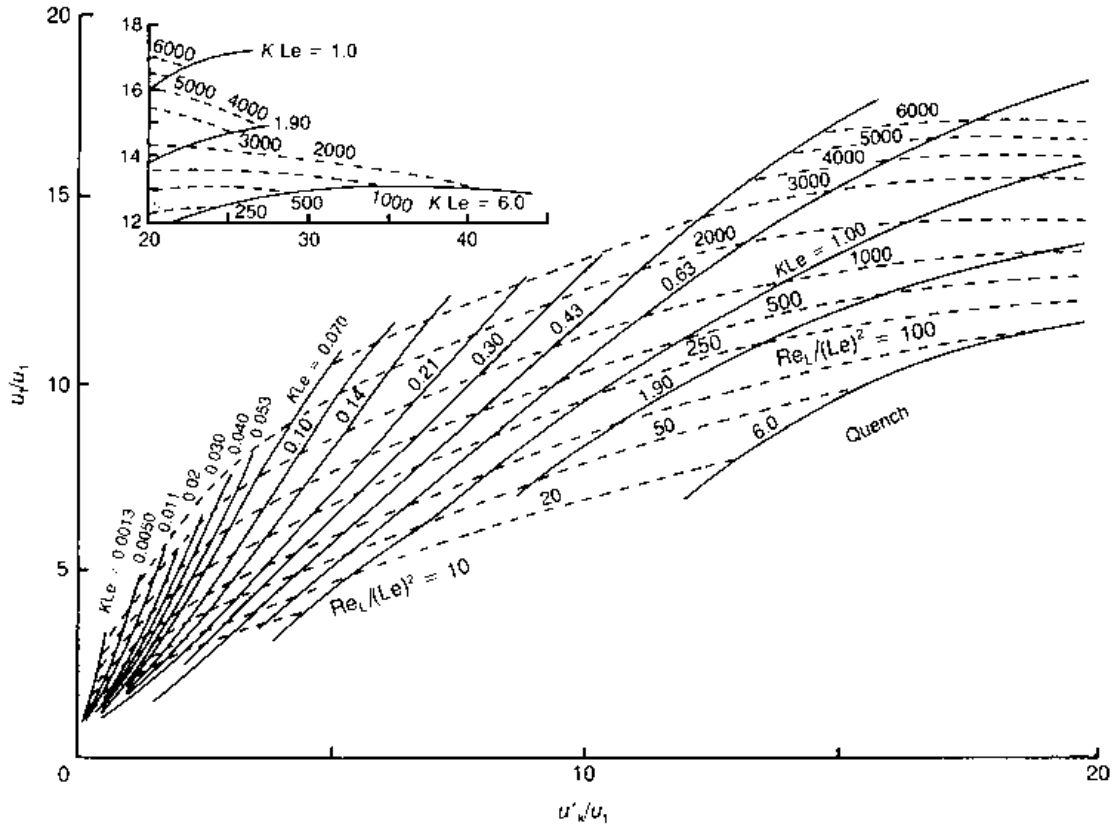


Figure 16.27 *Correlation for turbulent burning velocity (D. Bradley, Lau and Lawes, 1992) (Courtesy of The Royal Society)*

in which the value of A has been taken as 40.4, whilst the Lewis number Le is defined as

$$\mathrm{Le} = \frac{k}{c_p \rho D} \qquad [16.3.59]$$

where c_p is the specific heat of the gas, D is the diffusion coefficient of the deficient reactant, k is the thermal conductivity of the gas and ρ is the density of the gas. They also give the following limited-range relation:

$$\frac{u_t}{u'_k} = 0.88(K\mathrm{Le})^{-0.3} \qquad 0.01 < K\mathrm{Le} < 0.63 \qquad [16.3.60]$$

The correlation given makes use of the rms turbulent velocity u' and the effective rms turbulent velocity acting on the flame u'_k. Although in this work use was made of measured values, where necessary Abdel-Gayed and Bradley (1977) also used the relation

$$\frac{u'}{U} = 0.1676\mathrm{Re}^{-0.119} \qquad [16.3.61]$$

With regard to u'_k, this velocity is given mainly in terms of the ratio u'_k/u'. The treatment, described in detail by Abdel-Gayed and Bradley (1987), is complex, but at high turbulence the value of the ratio tends to unity.

The effect of pressure on turbulent burning velocity has been studied by Fine (1958), as already mentioned. He obtained for propane and hydrogen the relation

$$\frac{S_T}{S_L} \propto P^n \qquad [16.3.62]$$

where n is approximately 0.3.

Selected values of the turbulent burning velocity of various fuels are given by Abdel-Gayed and Bradley (1977).

Burning velocity is closely related to quenching distance, as described in the next section.

16.3.11 Quenching effects

Flame propagation may be extinguished by quenching. Such quenching may be due to heat loss to unburnt gas or to a solid surface. Quenching is closely related to several of the other properties already discussed. Explanations for the existence of flammability limits invoke quenching. There is a close inverse relation between burning velocity and quenching.

Quenching is of practical interest in a number of ways. The stabilization of flames on burners is related to quenching. The quenching effect is utilized in equipment designed to stop the passage of flame, such as flame-proof motors and flame arresters. The occurrence of unreacted fuel in car exhaust may be attributable to quenching.

For quenching in a gap between surfaces use is often made of the quenching distance d_q. This is sometimes used as a general term covering both the quenching diameter d_o and the critical slot width $d_\parallel$ and sometimes means only the latter.

Potter (1960) gives the relation between the quenching diameter d_o and the critical slot width $d_\parallel$ as

$$d_\parallel = 0.65 d_o \qquad [16.3.63]$$

A third quenching parameter is the depth of penetration of quenching d_p. This is defined as the ratio of the burning velocity to the critical boundary velocity gradient for flashback:

$$d_p = S_u / g_F \qquad [16.3.64]$$

The variation of these three quantities for flammable mixtures of natural gas and air is shown in Figure 16.28. The quenching diameter is the greatest dimension and the depth of penetration of quenching is the smallest.

Measurement of the quenching distance may be made by a number of methods. Reviews of these methods have been given by R. Friedman (1949) and Anagnostou and Potter (1959). Methods include those based on measurement of

(1) flame blow-off and stability;
(2) the critical distance between parallel plates;
(3) the critical tube diameter.

Extensive measurements of quenching distance have been made by Blanc, Guest, von Elbe and Lewis (1949).

There are a number of models and correlations for quenching distance. Drawing on earlier work by Mallard and Le Chatelier (1883), R. Friedman (1949) derived a quenching equation. Equating the heat generated to the heat lost to the walls, he obtained for the critical value of

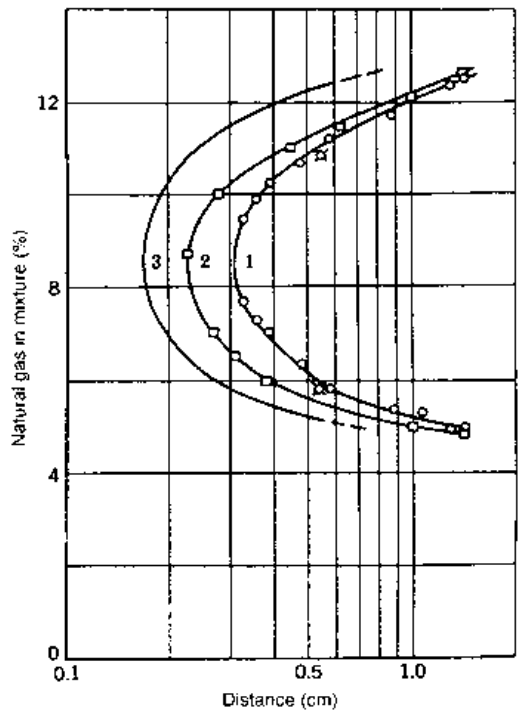


Figure 16.28 *Quenching parameters of burner wall for natural gas–air mixtures (B. Lewis and von Elbe, 1961) 1, quenching diameter d_o; 2, quenching distance $d_\parallel$; 3 depth of penetration, d_p (Courtesy of Academic Press)*

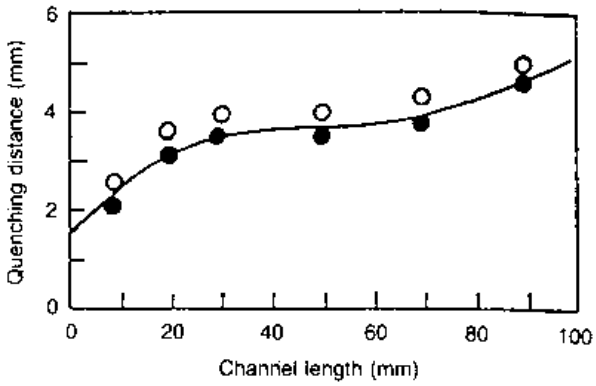


Figure 16.29 *Quenching distance in a rectangular duct (Maekawa, 1975) (Courtesy of Combustion Science and Technology)*

the quenching distance x

$$x = \frac{k}{S_u c_{pu}} \left[\frac{1}{f} \frac{(T_f - T_i)}{(T_i - T_o)} \right]^{\frac{1}{2}} \quad [16.3.65]$$

where c_{pu} is the specific heat of the unburnt gas, f is a geometrical factor of the order of unity, k is the thermal conductivity of the gas, T_f is the absolute flame temperature, T_i is the absolute ignition temperature and T_o is the absolute temperature of the unburned gas.

Some theories of quenching involve the Peclet number Pe defined as

$$\mathrm{Pe} = S_u d_q / \alpha_u \quad [16.3.66]$$

with

$$\alpha_u = k_u / \rho_u c_u \quad [16.3.67]$$

where α is the thermal diffusivity and subscript u denotes the unburned gas.

Equations 16.3.66 and 16.3.67 imply a constant value of the burning velocity–quenching product, which is also used by Potter and Berlad (1957).

$$\frac{d_q}{S_u} = \text{Constant} \quad [16.3.68]$$

Ballal and Lefbvre (1977) have attempted to correlate the quenching distance for turbulent flow conditions using

$$d_q = \frac{\mathrm{Pe}\ \alpha}{S_u} = A \quad [16.3.69]$$

where A is a constant, but found that it was necessary to modify this relation and proposed instead

$$d_q = A + 13\ \mathrm{Pr}^{-0.05} (u'/S_L)^{0.5} \quad [16.3.70]$$

Kydd and Foss (1964) emphasize the influence on quenching of three-dimensional effects.

The effect on quenching distance of gap length has been studied by several investigators. R. Friedman (1949) states that the quenching distance appears to depend not on gap length but on gap width only. On the other hand, Maekawa (1975) obtained for quenching in rectangular channels the relation

$$d_q = k_1 L \exp(-k_2 L) + k_3 L \quad [16.3.71]$$

where L is the gap length and k_1 to k_3 are constants.

Some results from this work are shown in Figure 16.29.

Mention should also be made of experiments by Wolfhard and Bruszak (1960) in which they investigated the propagation of flame down narrow tubes between two chambers. In experiments with methane the flame did not propagate through tubes of diameter less than 3 mm. But ignition could still occur in the outer chamber due to the jet of hot gases. Whether ignition did in fact occur depended on the properties of the jet. Very short channels were more effective in preventing ignition than were 10 mm long ones.

The effect of pressure on quenching distance has been studied by several workers including Brokaw and Gerstein (1957), Potter (1960) and Ballal and Lefebvre (1975a). The quenching distance increases with decreasing pressure.

Potter (1960) states that the quenching distance is approximately inversely proportional to pressure:

$$d_q \propto P^{-1} \quad [16.3.72]$$

This relation is in fact implied in the use of the Peclet number.

Practical quenching criteria such as the maximum experimental safe gap (MESG) were discussed in Section 16.2.

16.3.12 Cool flames

Certain compounds are capable of slow oxidation at mixture concentrations outside the normal flammability limits and at temperatures lower than those pertaining in normal combustion. Cool flames are of practical interest for several reasons. Much of the work done has been concerned with knock in internal combustion engines and also in jet engines. They are also of interest in relation to hydrocarbon oxidation in chemical reactors.

Cool flames were discovered by Sir Humphrey Davy and were studied by Perkin (1882), who found that they could be obtained with a wide variety of compounds, including hydrocarbons, alcohols and aldehydes. They were most easily demonstrated with diethyl ether and acetaldehyde. They were effectively rediscovered by Prettre, Dumanois and Lafitte (1930) and Townend and Mandlekar (1933).

Townend and co-workers carried out a series of studies on cool flames. The characteristics of such flames are illustrated by the work of Hsieh and Townend (1939a–c). The concentration region within which cool flames occur is illustrated by the results for hexane–air mixtures obtained by Hsieh and Townend (1939b), as shown in Figure 16.30(a). They state:

> Reference to the results at 1500°C shows that at pressures up to 4.1 atm there was only one range of inflammable mixtures, viz. that for normal flames. This was at first unaffected by increase in initial pressure, the lower limit being lower by about 0.3% and the higher limit raised by about 1% of hexane at pressure up to 4 atm. At a pressure of 4.1 atm a cool flame range was located with mixtures of composition between 11 and 22% of hexane, the normal range at the same pressure extending over mixtures of hexane content between 1.2 and

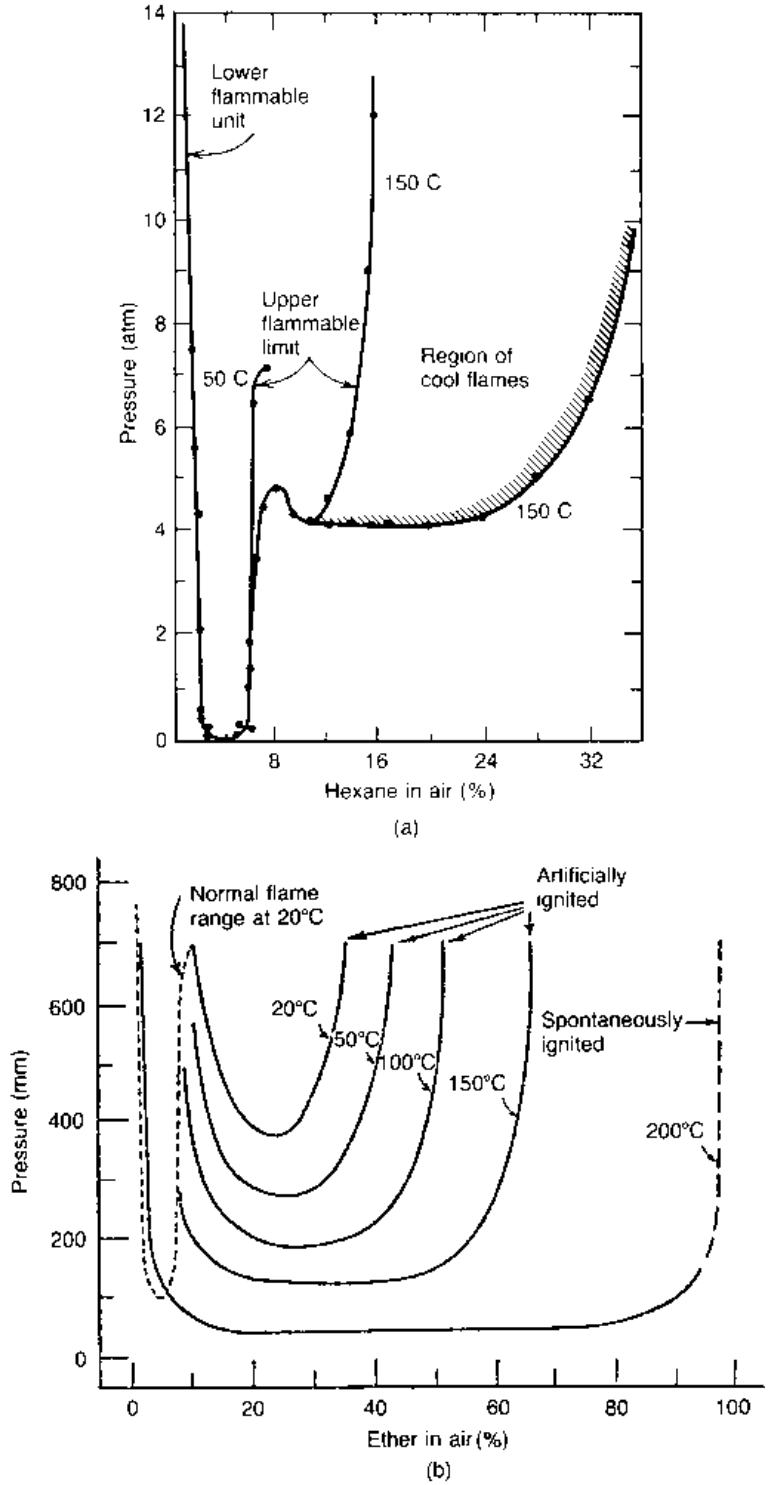


Figure 16.30 *Effect of pressure on cool flame ranges: (a) cool flames of hexane–air mixtures (after Hsieh and Townend, 1939b); and (b) cool flames of ether–air mixtures (after Hsieh and Townend, 1939a). Latter shows ignition both by ignition source and by bulk gas ignition (Courtesy of the Chemical Society)*

7.0%. The 'normal' and 'cool' flame ranges were thus separated by a range of non-flammable mixtures containing between 7 and 11% of hexane. At pressures higher than 4.8 atm the two ranges of inflammability became superposed so that at, e.g. 6.5 atm, mixtures containing between 1 and 14.5% of hexane were capable of propagating 'normal' flames and those between 14.5 and 32% 'cool' flames.

Hsieh and Townend (1939a) also investigated the ignition of cool flames both by spontaneous ignition and by hot wire ignition in order to establish that the cool flame process is the same in both modes. Their results for ether–air mixtures are shown in Figure 16.30(b).

The results of cool flame experiments may also be presented as an ignition diagram in which the regions of the different modes of combustion are shown on a plot of temperature vs pressure for a given mixture composition. An ignition diagram for a propane–oxygen mixture given by Newitt and Thornes (1937) is shown in Figure 16.31. Ignition diagrams for a number of compounds have been given by Townend (1937). A characteristic feature of an ignition diagram is the peninsular region. Apart from its practical significance, the diagram provides a test of theories for cool flames.

Cool flames are associated with a negative temperature coefficient for the overall combustion over a limited range of temperature, as illustrated by the data shown in Figure 16.32 for the reaction rate of propane and oxygen obtained by Seakins and Hinshelwood (1963). The negative temperature coefficient is discussed by Knox, who interprets it as evidence of a fundamental change from one reaction mechanism to another.

Interpretations of cool flames in terms of the reaction kinetics have been undertaken by a large number of workers. Reviews are given by von Elbe and Lewis (1937a), Ashmore (1967) and Knox (1967a).

Von Elbe and Lewis (1937b) review the theories of Norrish and Foord (1936), Ubbelohde (1935, 1936), Jost, von Müffling and Rohrmann (1936), Pease (1935), Semenov (1935) and von Elbe and Lewis (1937a). They discuss the role of unbranched and branched chain reactions and of the intermediate aldehydes and peroxides formed.

Thermal and isothermal theories of cool flames have been proposed by Semenov (1935) and are discussed by Ashmore (1967). In the thermal theory, which applies both to unbranched and branched chain reactions, a rapid increase in reaction rate occurs as a result of self-heating, whilst in the isothermal theory, which applies to branched chain reactions only, the reaction rate increases as a result of exponential growth in the chain centres at the end of an isotherm induction period.

A series of investigations of pre-flame and ignition behaviour and of cool flames has been carried out by Barnard and co-workers (e.g. Barnard and Ibberson, 1965; Barnard and Kirschner, 1967; Barnard and Sankey, 1968; Barnard and Watts, 1972; Barnard and Harwood, 1973a) and by Salooja (1966, 1967, 1968a,b).

A feature of cool flames is the occurrence of multiple flames, one after the other. Coffee (1982b) quotes observation of up to 11 cool flame zones.

The periodicity of cool flames is another feature which is of theoretical interest. Attempts have been made to apply to cool flames the theory developed by Lotka (1920) for essentially biological phenomena, which for certain conditions predicts oscillations in the concentration of intermediate species. This aspect is discussed by B.F. Gray and Yang (1969).

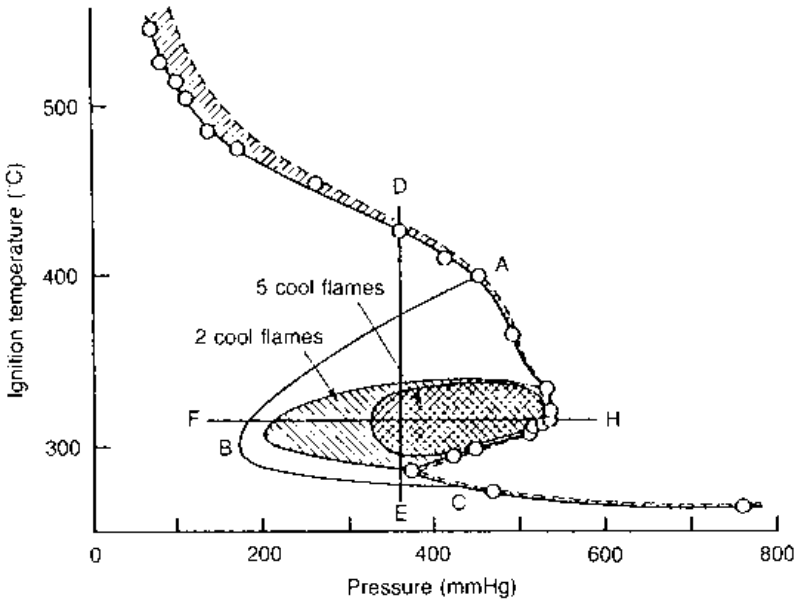


Figure 16.31 *Ignition diagram for equimolar concentration of propane and oxygen, showing effect of pressure on ignition temperature and cool flame ranges (Knox, 1967a; Newitt and Thornes, 1937) (Courtesy of Cambridge University Press)*

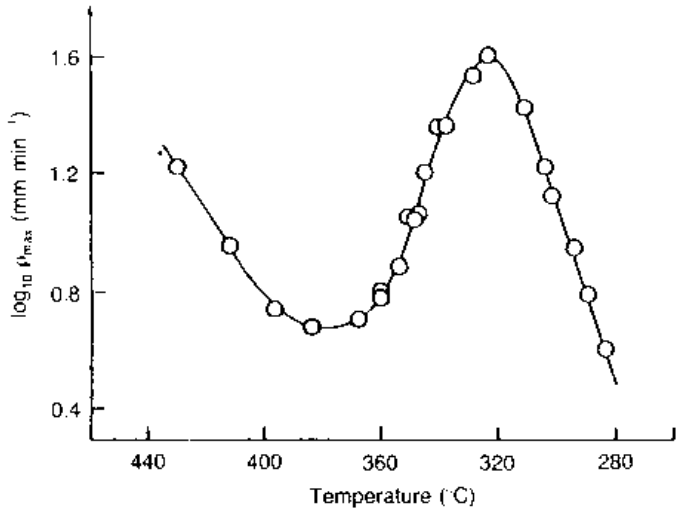


Figure 16.32 *Effect of temperature on reaction rate for oxidation of propane, illustrating negative temperature coefficient (Knox, 1967a; after Seakins and Hinshelwood, 1963) ρ_{max}, maximum pressure (mm Hg) (Courtesy of Cambridge University Press)*

Cool flames exhibit an ignition delay, or induction period. Studies of ignition delay in cool flames include those of J.E. Johnson, Crellin and Carhart (1954), Fish (1968) and Barnard and Watts (1972). Fish obtained for the variation of ignition delay with pressure the relation

$$\tau = kP^{-n} + c \qquad [16.3.73]$$

where P is the absolute pressure, τ is the ignition delay, c and k are constants and n is an index.

Cool flames result in rises in pressure and temperature, but these are more modest than with normal combustion. Correlations for pressure and temperature effects are given by Fish (1968) and by Luckett and Pollard (1973). For the pressure rise Fish found

$$\Delta P_{cf} = kP_o^m \qquad [16.3.74]$$

where P_o is the absolute initial pressure, ΔP_{cf} is the pressure rise for a cool flame, k is a constant and m is an index. The value of the index m was $1 < m < 2$.

The temperature rise was found by Fish to be a function of the oxygen concentration of the mixture. For low oxygen concentrations the rise in temperature corresponded closely to the rise in pressure, assuming the ideal gas law.

Cool flames in mixtures have been studied by Salooja (1968b). He found that for binary mixtures two different types of behaviour could be distinguished: those cases for which the ignition tendency is (1) intermediate between those of the two compounds and (2) even greater than that of the more ignitable component.

The features of cool flames have been compared with those of normal flames by Coffee (1982b) as follows:

	Normal flames	*Cool flames*
ΔT_{cf}	800–2000°C	1–200°C
P_{cf}/P_o	6–10 (confined spaces)	Low (<2)
Products	CO_2, H_2O	CO, CH_2O

[a] P_{cf}, absolute final pressure of cool flame; P_o, absolute initial pressure; ΔT_{cf}, temperature rise for cool flame

16.3.13 Combustion in tubes

The behaviour of flames in tubes has been extensively studied. Early work was carried out by Mallard and Le Chatelier (1883) and by Wheeler and co-workers, the latter including the work by Mason and Wheeler (1917, 1920a–c), Chapman and Wheeler (1926, 1927), Ellis (1928), Ellis and Wheeler (1925, 1928a,b), Kirby and Wheeler (1931a,b) and H. Robinson and Wheeler (1933).

Much work on combustion in tubes has dealt with detonation, and with the transition from deflagration to detonation; this is considered in Chapter 17. There is also, however, a body of work which is concerned with the more general aspects of combustion in tubes, including tubes containing obstacles, in respect of features such as vibratory oscillations, flame acceleration, pressure rise and so on.

Such work includes *Non-Steady Flame Propagation* by Markstein (1964) and that by M.W. Evans *et al.* (1949), Schmidt, Steinicke and Neubert (1953), Guenoche (1964), Leyer and Manson (1971), Andrews, Herath and Phylaktou (1990) and Phylaktou, Andrews and Herath (1990).

Some of the findings of this work have been reviewed by the latter authors. They consider four cases: Case 1, a tube open at one end with ignition at the open end; Case 2, a tube open at one end with ignition at the closed end; Case 3, a tube open at both ends; and Case 4, a tube closed at both ends.

Case 1 appears to provide the simplest propagation conditions and has been the most widely investigated. After a short initial phase, the flame propagates for some distance at a fairly constant velocity. This phase is sufficiently prolonged to permit measurement of the burning velocity. As the flame progresses, there begin vibrations of the combustion surface which can turn into violent oscillations. Towards the end of the tube the flame velocity falls rapidly to a roughly constant value.

In Case 2 the flame accelerates rapidly and develops violent vibrations. In the work of Mason and Wheeler

(1920a,b), using a long tube, this resulted in extinction of the flame.

In Case 3 the behaviour of the flame is somewhat similar to that in Case 1, with a short initial phase followed by propagation at a higher velocity, since the unburned gas can be pushed out of the open end. In this phase there is a slight acceleration. Vibration begins and the velocity increases, either with smooth acceleration or with oscillations.

In Case 4 with ignition at one end it was found by Kirby and Wheeler (1931b) that initially the flame accelerated rapidly, then decelerated and travelled at a comparatively low speed until it approached the far end, when it accelerated somewhat. The time of attainment of maximum pressure coincided with that of the arrival of the flame at this end.

Phylaktou, Andrews and Herath (1990) describe experiments on the Case 4 configuration using a pipe with a length/diameter (*L/D*) ratio of 21.6 with a wide range of gas concentrations and a variety of gases. All gases exhibited two distinct regimes: vibratory near the stoichiometric concentration and non-vibratory near the limits of flammability. In the near-limit mixtures the flame speeds were higher than those in the stoichiometric mixtures, and the initial rates of pressure rise were high. For the near stoichiometric mixtures vibration was found to enhance the rate of pressure rise.

Further accounts of combustion in pipes, and also in vessels, as well as treatment of detonation are given in Chapter 17.

16.4 Flammability of Aerosols

It is also relevant to consider the combustion of aerosols such as fogs, mists and sprays. Such aerosols may be produced by condensation of a saturated vapour or by atomization of liquid by mechanical forces. The former may be referred to as a condensed fog or mist and the latter as a mechanical spray. Normally in a condensed mist the diameter of most of the drops is less than $10\,\mu$m, while in a mechanical spray it is greater than $100\,\mu$m.

Accounts of the combustion of aerosols, particularly liquid sprays, include *Combustion of Liquid Fuel Sprays* (A. Williams, 1990) and those by F.A. Williams (1959), Faeth (1977, 1979, 1983) and Kuo (1986).

A large proportion of work in this field is directed towards the combustion of atomized fuels at burners in furnaces and boilers. Some of the work deals with the combustion of single droplets of fuel, and some deals with the combustion of an aerosol cloud.

16.4.1 Combustion of aerosols

A suspension of finely divided droplets of flammable liquid in air can give a flammable mixture which has many of the characteristics of a flammable gas–air mixture and which can burn or explode. The combustion of aerosols has been the subject of a series of studies by Burgoyne and co-workers (Burgoyne and Richardson, 1949b; Burgoyne and Cohen, 1954; Burgoyne, Newitt and Thomas, 1954; Burgoyne, 1957, 1963).

In classic experiments using aerosols of tetrahydronaphthalene, or tetralin, with droplets of closely controlled diameter in the range 7–55 μm, Burgoyne and Cohen (1954) found that below a droplet diameter of $10\,\mu$m, the aerosol behaved like a vapour in respect of the lower flammability limit and the burning velocity. With a droplet diameter above $40\,\mu$m, the behaviour of the aerosol was different. The droplets were observed to burn individually in their own air envelopes, one burning droplet igniting the next.

If the droplet size, and hence the distance between droplets, exceeds a critical value, the flame does not propagate. The critical distance is of the same order of magnitude as the radius of the sphere of air required for the combustion of a droplet.

Coarser aerosols are capable of sustaining a flame at substantially lower fuel–air ratios than fine aerosols and vapours. The difference lies in the ability of the droplets to move in relation to the ambient air. Coarse particles are responsive to acceleration and move randomly, and thus communicate flame more readily.

Burgoyne's work has also shown that the burning velocity and the quantity of inert gas required for the suppression of flammability in aerosols with small droplet diameters are those of the equivalent vapour–air mixture.

In addition to this work on the conditions for combustion to occur in an aerosol, there have been other studies which have investigated the behaviour and shape of the flame in an droplet cloud. The studies include those by J.A. Browning and Krall (1955), J.A. Browning, Tyler and Krall (1957), Reichenbach, Squires and Penner (1962), Rosser (1967), Mizutani and Nishimoto (1972), Mizutani and Nakajima (1973), Polymeropolous (1974, 1984), Hayashi and Kumagai (1975), Polymeropoulos and Das (1975) and Ballal and Lefebvre (1978, 1979, 1981a).

Another aspect of the combustion of aerosols which has been actively investigated is ignition and extinction. Work on this topic has been described by Polymeropoulos and Peskin (1969), Kapila, Ludford and Buckmaster (1975), Law (1975) and Pindera and Brzustowski (1984).

The explosion of aerosols of flammable liquids is considered in Chapter 17.

16.4.2 Burning of single droplets

The combustion of the individual liquid droplets of an aerosol has been the subject of a good deal of work, particularly in relation to spray combustion in gas turbines and rockets.

Work on this topic includes that by Godsave (1953), Hottel, Williams and Simpson (1955), Kobayasi (1955), Agoston, Wise and Rosser (1957), Bolt and Saad (1957), Wise and Agoston (1958), Aldred and Williams (1966), Eisenklam and Arulachanam (1966), Faeth (1967), Sioui and Roblee (1969) and Yule, Ereaut and Ungut (1983). Reviews are given by A. Williams (1973, 1990).

Research in this area includes work on: the formation of droplets by atomization and other mechanisms, and the size distribution and velocities of the droplets produced; the evaporation of and the drag on the droplets; and the mass burning rate of the droplets.

The mass burning rate $\dot{m}_F$ of a liquid droplet is

$$\dot{m}_F = -\frac{d}{dt}\left(\frac{\pi}{6} d_L^3 \rho_L\right) \qquad [16.4.1]$$

where d_L is the diameter of the droplet and ρ_L is the density of the liquid. This equation can be rearranged to give

$$-\frac{d}{dt}(d_L)^2 = \frac{4\dot{m}_F}{\pi d_L \rho_L} \quad [16.4.2]$$

It is found experimentally that

$$-\frac{d}{dt}(d_L)^2 = K \quad [16.4.3]$$

where the constant K is known as the burning constant. This constant is therefore

$$K = \frac{4\dot{m}_F}{\pi d_L \rho_L} \quad [16.4.4]$$

There are a number of correlations of the burning constant, predominantly for conditions of forced convection, as in spray combustion. One of the most widely used is that of Wise and Agoston (1958).

16.4.3 Flammability limits

The flammability limits of the aerosols of flammable liquids have been studied by Burgoyne and co-workers, as described above. Burgyone (1963) quotes early work by Haber and Wolff (1923), who obtained for the lower flammability limit the results shown in Table 16.22.

As already described, Burgoyne and Cohen (1954) found in their studies on tetralin a difference in behaviour between aerosols with a droplet diameter d_L less than 10 μm and those with a droplet diameter more than 40 μm. The lower flammability limits were found to be 46 mg fuel/l of aerosol for $d_L < 10\,\mu$m and 18 mg fuel/l of aerosol for $d_L > 40\,\mu$m; for intermediate diameters the lower flammability limits change linearly between these two concentrations.

For aerosols in which the droplet diameter is less than 10 μm the lower flammability limit of the liquid and vapour suspension is virtually the same as that of the substance wholly in vapour form at the somewhat higher temperature necessary for vaporization. Above a droplet diameter of 10 μm the lower limit of flammability decreases as the drop diameter increases.

Above a droplet diameter of 20 μm another phenomenon was identified as significant, namely the rate of sedimentation of the droplet. For this effect Burgoyne (1963) gives the following treatment. He defines a flame front concentration C_f which is related to the volumetric concentration C_v as follows:

$$\frac{C_f}{C_v} = \frac{V_f + V_a + V_s}{V_f + V_a} \quad [16.4.5]$$

where C_f is the volumetric flame front concentration, C_v is the volumetric concentration, V_a is the downward velocity of the air, V_f is the upward velocity of the flame through the suspension and V_s is the sedimentation velocity of the drops relative to the air.

The lower flammability limit concentrations obtained by experiment were close to the flame front concentrations as defined by Equation 16.4.5. In some experiments with larger drop diameters the lower flammability limit measured was less than one-tenth of that for the equivalent vapour–air mixture. The burning velocity and the quantity of inert gas required for the suppression of flammability are also affected by large drop sizes.

In general, for flammable aerosols in air, it is found that for small droplet diameters the lower flammability limits, measured as mass of fuel per unit volume of aerosol, are similar to those for vapour–air mixtures. Some values of the lower flammability limits of vapours are quoted by Burgoyne (1963). For most of the substances which he lists the lower flammability limit of the vapour lies in the range 0.04–0.10 g/l (or oz/ft^3). Further details are given in Section 16.2.

16.4.4 Minimum ignition energy

A method of obtaining the minimum ignition energy of a dust cloud which is also applicable to a vapour and an aerosol has been given by Ballal (1983b). Ballal has correlated minimum ignition energies for a number of mixtures of gases, vapours, liquid droplets and dusts with air at atmospheric pressure, the size of the liquid and solid particles being of the order of 50 μm. The correlation is in terms of the Spalding mass transfer number B:

$$B = \frac{q_{st}H + c_{pa}(T_g - T_b)}{L + c_p(T_b - T_s)} \quad [16.4.6]$$

where c_p is the specific heat of the fuel, c_{pa} is the specific heat of air, H is the heat of combustion, L is the latent heat of vaporization, q is the mass ratio of fuel to air, and subscripts b, g, s and st denote the boiling point of the fuel, gas, the surface of the fuel and stoichiometric, respectively.

Figure 16.33(a) gives an approximate relation between the minimum ignition energy E_{min} and B for homogeneous and two-phase mixtures of the type described. For a more accurate estimate Ballal gives the minimum ignition energy E_{min} as a function of the quenching diameter d_q:

$$E_{min} = \pi c_p \rho_a \Delta T d_q^3 \quad [16.4.7]$$

Table 16.22 *Lower flammability limits of some vapours and mists in air (after Haber and Wolff, 1923)*

	Temperature (°F)	*Mist concentration* (oz/ft^3)	*Temperature* (°F)	*Vapour concentration* (oz/ft^3)
Petroleum 356–428°F	75	0.044	140	0.043
Tetralin	84	0.0409	212	0.0416
Quinoline	97	0.0662	230	0.064

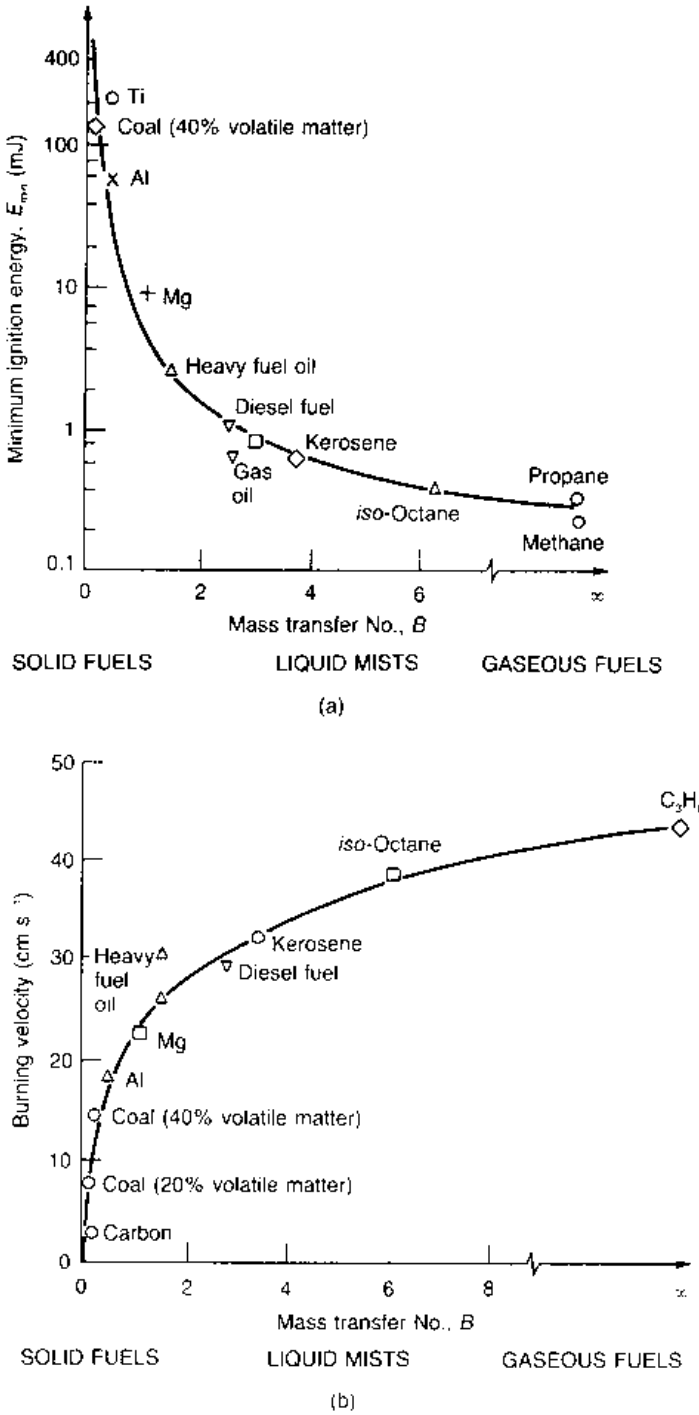


Figure 16.33 *Some properties of mixtures of air with flammable vapours, aerosols or dusts: (a) minimum ignition energy (after Ballal, 1983b) (Courtesy of Combustion and Flame); and (b) fundamental burning velocity (after Ballal, 1983a) (Courtesy of the Combustion Institute)*

with

$$d_q = (8\alpha)^{\frac{1}{2}} \left\{ \left[\frac{C_3^3 \rho_p D_{32}^2}{8 C_1 f^2 (k/c_p) \phi \ln(1+B)} + \frac{12.5\alpha}{S_u^2} \right]^{-1} - \frac{9 q C_1^2 \epsilon \sigma T_p^4}{c_p \rho_p C_3^3 f D_{32} \Delta T_{st}} \right\} \quad [16.4.8]$$

where c_{pg} is the specific heat of the gas, C_1 is the ratio of the surface mean area to the Sauter mean diameter, C_3 is the ratio of the volume mean diameter to the Sauter mean diameter, D_{32} is the Sauter mean diameter, f is the swelling factor of the fuel, k is the thermal conductivity of the fuel, S_u is the laminar burning velocity, α is the thermal diffusivity of the particle, ϵ is the emissivity of the particle, ρ is the density, ΔT is the temperature difference, σ is the Stefan–Boltzman constant, ϕ is the equivalence ratio and subscript p denotes fuel.

16.4.5 Burning velocity

Ballal (1983a) has also given a method of obtaining the laminar burning velocity of a dust cloud which is also applicable to a vapour and an aerosol. Figure 16.33(b) gives an approximate relation between laminar burning velocity S_u and B for homogeneous and two-phase mixtures. For a more accurate estimate Ballal gives the laminar burning velocity as a function of the thickness δ_r of the reaction zone:

$$S_u = \frac{\alpha \Delta T_r}{\delta_r \Delta T_{pr}} \quad [16.4.9]$$

with

$$\delta_r = \alpha_g^{0.5} \left\{ \left[\frac{C_3^3 \rho_f D_{32}^2}{8 f^2 C_1 (c_p/k)_g \phi \ln(1+B)} + \frac{\alpha \Delta T_r}{S_g^2 \Delta T_{pr}} \right]^{-1} - \frac{9 q C_1^2 \epsilon \sigma T_p^4}{c_{pg} \rho_f C_3^3 f D_{32} \Delta T_r} \right\}^{-0.5} \quad [16.4.10]$$

where c_{pg} is the specific heat of the gas, S_g is the laminar burning velocity of the gases liberated from the particles, α_g is the thermal diffusivity of the gas, and subscripts f, g, pr and r denote the fuel, gas, pre-reaction zone and reaction zone, respectively.

These correlations of Ballal are subject to a number of qualifications, as discussed by the author and by Nettleton (1987), who nevertheless concludes that the approach is applicable to many practical situations. Nettleton quotes some typical ranges of the laminar burning velocity S_u in air. These are: $0.05 < S_u < 0.2$ m/s for particulate suspensions; $0.2 < S_u < 0.35$ m/s for fogs; $0.3 < S_u < 0.4$ m/s for hybrid fog and vapour; and $S_u < 0.5$ m/s for mixtures with gas or vapour. For stoichiometric mixtures of acetylene or hydrogen in air, $S_u > 1.0$ m/s. For the estimation of turbulent burning velocity, Nettleton quotes Equation 16.3.45 as one in common use.

16.4.6 Chemical decomposition

If a condensed mist is formed from the saturated vapour of a liquid hydrocarbon of high boiling point, prolonged contact with a source of heat can result in the formation of cracking products such as hydrogen or acetylene, which reduce the lower flammability limit and increase the burning velocity and the quantity of inert gas required for the suppression of flammability.

16.5 Ignition sources

Selected references on ignition sources are given in Table 16.23.

Table 16.23 *Selected references on ignition and ignition sources*

D.J. Lewis (n.d.); SMRB (Pap. 74); von Elbe and Lewis (1949); von Elbe (1953); Khitrin and Goldenberg (1957); H.E. Rose and Priede (1959a); F. Powell (1960); Risinger and Vervalin (1964); SMRE (1965 Res. Rep. 231); FMEC (1967); FPA (1971/14); J.F. Griffiths, Gray and Gray (1971); Page and Gardner (1971); Dehn (1972); K.N. Palmer (1973a, 1976b); Dixon-Lewis and Shepherd (1975); Eisenberg, Lynch and Breeding (1975); Japan Gas Association (1976); Kletz (1977i); Birch, Brown and Dodson (1981); IBC (1981/9, 19, 1982/36, 1991/81); Dold and Clarke (1985); Fordham Cooper (1986); Vilyunov and Zarko (1989); Bond (1991)

Ignition induction period, time delay
SMRB (1925 Pap. 9); Mullins (1949); Brokaw and Jackson (1955); Ashmore and Levitt (1959); P. Gray and Harper (1959a,b); R.E. Miller (1959); Voevodsky (1959); Salooja (1961); Melvin (1966); Bascombe (1967); Burcat, Scheller and Lifschitz (1971); Drysdale (1971); Bowes (1984); Freeman and Lefebvre (1984)

Spontaneous ignition
Khitrin and Goldberg (1957); Sage and Weinberg (1959); Sokolik (1960); J.A. Macdonald and White (1965); Melvin (1966); Goodman, Gray and Jones (1972); Cullis and Foster (1973, 1974); Anon. (1982 LPB 47, p. 15); Bowes (1984); Reid, Robinson and Smith (1985); Gandhi and Kanury (1988)

Compression ignition, shock ignition
Falk (1906, 1907); Dixon (1910); Dixon, Bradshaw and Campbell (1914); Dixon and Crofts (1914); Tizard and Pye (1922); Dixon, Harwood and Higgins (1926); Payman and Titman (1935); SMRB (1935 Pap. 93); Wheeler (1935b); Payman and Shepherd (1937, 1946); Jost (1949); W.C.F. Shepherd (1949); M.H. Friedman (1963a,b); Borisov, Kogarko and Lyubimov (1968); J.W. Meyer and Oppenheim (1971b); Vermeer, Meyer and Oppenheim (1972); Halstead *et al.* (1975); Anon. (1978 LPB 19, p. 24); Beeley, Griffiths and Gray (1980); Eubank *et al.* (1981); J.F. Griffiths and Perche (1981)

Chemical ignition
Bretherick (1979)

Friction and impact
SMRE (Appendix 28 *Research Reports*, Frictional Ignition 2–5); SMRB (1928 Pap. 46, 1929 Pap. 54, 1930 Pap. 62, 1931 Pap. 70); Burgess and Wheeler (1929); Bowden, Stoke and Tudor (1947); Bowden (1949); Archard (1952); Calcote *et al.* (1952); Bowden and Tabor (1954); Bowden and Thomas (1954); Titman and Wynn (1954); Titman

(1955/56); Rae (1961); M.H. Friedman (1963a,b); Downing (1964); N. Gibson, Lloyd and Perry (1967); F. Powell (1969, 1978); Cutler (1974, 1978); Blickensderfer (1975); Andersen (1979); HSE (1980 FI 2); Billinge (1981); Gomez, Wake and Gray (1985); Bartknecht (1988)
Hand tools, non-sparking tools: Anfenger and Johnson (1941); API (1956, 1980 PSD 2214, 1989 Publ. 2214); Bernstein and Young (1960); Anon. (1962e); DSIR (1963); Fischer (1965); Riddlestone and Bartels (1965); F. Powell (1969); Bartels (1970); FPA (1975 S11, 1989 CFSD FS 6029)

Electrical discharges and sparks
Coward, Cooper and Jacobs (1914); Thornton (1914a,b, 1915a,b); Wheeler (1920, 1924); Bradford and Finch (1937); Landau (1937a,b); Blanc *et al.* (1947); Llewellyn (1947–48); Blanc *et al.* (1949); H. Morris (1949); Fenn (1951); Calcote *et al.* (1952); Laffitte and Delbourgo (1953); Olsen, Gayhart and Edmondson (1953); Swett (1955, 1956, 1957); H.E. Rose and Priede (1959b); Berz (1961); SMRE (1966 Res. Rep. 240); Johnsson, Strid and Johansson (1972); Kumagai, Sakai and Yasugahira (1972); Kono, Kumagai and Sakai (1976); Adelman (1981); Ballal and Lefebvre (1981b); Maly (1981); Sher and Rafael (1982); Fiumara and Avella (1983); FPA (1984 CFSD NB 6); H. Kramer (1987); Ko, Anderson and Arpaci (1991); Ko, Arpaci and Anderson (1991)
Flashlights: API (1983 Publ. 2212)
Telephones: API (1974 PSD 2213)

Hot wires
J.H.T. Roberts (1913); Thornton (1919); SMRB (1927 Pap. 36); Stout and Jones (1949); Kumagai and Kimura (1957); Ashman and Büchler (1961); Detz (1976)

Hot surfaces
Mason and Wheeler (1922, 1924); Coward and Guest (1927); Guest (1930 BM Tech. Pap. 475); Naylor and Wheeler (1931, 1933); Landau (1937a,b); Mullen, Fenn and Irby (1949); Dooley (1957); Husa and Runes (1963); Kuchta, Cato and Zabetakis (1964); SMRE (1964 Res. Rep. 224); Adomeit (1965); Kuchta, Bartowiak and Zabetakis (1965); Goodall and Ingle (1967); Sharma and Sirignano (1969, 1970); Bartels (1971a); Alkidas and Durbetaki (1973); K.N. Palmer (1973a); Angel (1975); D.C. Bull and Grant (1975); D.C. Bull and Quinn (1975); Thiyagarajan and Hermance (1975); Ono *et al.* (1976); D.C. Bull (1977); Law (1978); Law and Law (1979); API (1980 PSD 2216, 1991 Publ. 2216); Chen and Faeth (1981a); Trevino and Sen (1981); Laurendeau (1982); Laurendeau and Caron (1982); F. Powell (1984); Leiber (1985); Bartknecht (1988); A.J. Harrison and Cairnie (1988); A.J. Harrison *et al.* (1988); Bothe and Steen (1989); Kumar (1989); Giesbrecht *et al.* (1992)

Hot gases
Mullins (1953); Wolfhard (1958); Wolfhard and Vanpee (1959); Vanpee and Bruszak (1973 BM RI 6293); Fink and Vanpee (1975)

Hot particles
Silver (1937); Paterson (1939–); SMRE (1956 Res. Rep. 129); Tolson (1972); Su, Homan and Sirignano (1979); Yu-Pen Su and Sirignano (1981); F. Powell (1984); Hills *et al.* (1992)

Hot projectiles
Sharma and Sirignano (1970)

Flame torches and jets
FPA (CFSD GP 4); Wang *et al.* (1981); Mackay *et al.* (1988)

Smoking
FPA (1989 CFSD GP 8)

Diesel engines
HSE (1986 PM 58); Sokolov (1989)

Lightning
Golde (1977a); W.R. Lee (1977); Anon. (1987q); NFPA (1989 NFPA 78)

Hygroscopic combustible materials
P. Gray and Wake (1990)

Sodium
Yuasa (1985)

Metal oxides
Meguerian and Radowsky (1967)

Welding (*see* Table 21.1)

RF ignition
Jordan and Balmain (1968); Anon. (1978 LPB 23, p. 147); Excell and Howson (1978); HSE (1978a, 1979f, 1983 GS 21); A. Hall and Burstow (1980); A. Hall and Loveland (1980); ERA (1981, 1982); Burstow *et al.* (1981); Howson, Excell and Butcher (1981); Maddocks and Jackson (1981); S.J.J. Robertson and Loveland (1981); Rosenfeld *et al.* (1981); Bergman (1982); Mannon and Johnson (1982); Widginton (1982); Excell and Maddocks (1984); P. Knight and Robson (1984); Harrold (1992 SRD R579)

Laser ignition
Hills *et al.* (1992)

Arson
FPA (CFSD AR series, 1972/19); J. Kennedy (1962); NFPA (1971/7); Broodo, Gilmore and Armstrong (1976); French (1979); Hanson (1980); Carson and Mumford (1986 LPB 70)

Piloted ignition
Tzeng, Atreya and Wichman (1990)

Ignition of gas clouds, jets
M.T.E. Smith *et al.* (1986); Gustafson and Mudan (1987)

Ignition of sprays
Aggarwal and Cha (1988); Capp (1988); Aggarwal (1989); Bergeron and Hallett (1989a,b)

Ignition models
English and Waite (1989); A.W. Cox, Lees and Ang (1990)

Some potential ignition sources on process plants include the following:

(1) flames;
(2) hot work;
(3) hot surfaces;
(4) hot particles;
(5) friction and impact;
(6) chemical energy;
(7) hot materials and gases;
(8) reactive, unstable and pyrophoric materials;
(9) engines;
(10) vehicles;
(11) lightning;
(12) radio frequency emissions;
(13) smoking;
(14) arson and sabotage;
(15) self-heating;
(16) static electricity;
(17) electrical equipment.

Each of the above sources can cause ignition of a flammable gas–air mixture outside the plant.

Insofar as they can occur inside the plant, these sources can also cause ignition of a flammable gas–air mixture inside it. In addition, ignition of a flammable gas–air mixture inside the plant may occur due to:

(18) autoignition
(19) compression effects.

Table 16.24 gives a more detailed breakdown of these ignition sources.

These ignition sources are discussed in this section, with the exception of self-heating, static electricity and electrical equipment, which are considered in Sections 16.6, 16.7 and 16.8, respectively. Information on the most frequent sources of ignition was given in Table 2.11.

The modelling of ignition sources for the purpose of hazard assessment is considered in Section 16.10.

Many potential sources of ignition are associated with activities. These need to be controlled by a permit-to-work system. This aspect is discussed in Chapter 21.

The area of flammable hazards should be fenced off and strict security enforced on persons entering the area. In particular, matches and cigarette lighters should be given up on entry. Equipment brought into the area should be suitable for use within it.

16.5.1 Flames

The flames of burners in fired heaters and furnaces, including boiler houses, may be sources of ignition on process plants. The source of ignition for the explosion at Flixborough may well have been burner flames on the hydrogen plant. The flame at a flare stack may be another source of ignition. Such flames cannot be eliminated. It is necessary, therefore, to take suitable measures such as care in location and use of trip systems.

Burning operations such as solid waste disposal and rubbish bonfires may act as sources of ignition. The risk from these activities should be reduced by suitable location and operational control.

Smouldering material may act as a source of ignition. In welding operations it is necessary to ensure that no smouldering materials such as oil-soaked rags have been left behind.

Small process fires of various kinds may constitute a source of ignition for a larger fire. The small fires include pump fires and flange fires; these are dealt with in Section 16.11.

Dead grass may be set alight by the rays of the sun and should be eliminated from areas where ignition sources are not permitted. Sodium chlorate is not suitable for such weedkilling, since it is a powerful oxidant and is thus itself a hazard.

16.5.2 Hot work

Hot work, such as welding, cutting and grinding activities, is a potential source of ignition. In welding, for example, this applies not only to the welding flame or arc but also to material ignited by the welding.

Hot work accounts for an appreciable proportion of ignition incidents. In the vast majority of cases the material ignited is in the equipment being worked on. It is relatively rare for hot work to be the source of ignition of a vapour cloud.

It is necessary to exercise close control of hot work by training, supervision and use of a permit system.

16.5.3 Hot surfaces

Surfaces of plant equipment are frequently hot and some may be potential ignition sources. Hot surfaces include:

(1) hot process equipment;
(2) distressed machinery.

Much process equipment operates at high temperature. Although the equipment is usually lagged, there may be some surfaces which could be a source of ignition.

Machinery in distress, such as a pump with a faulty bearing, may run hot and this hot spot is a potential source of ignition.

Traditionally, the autoignition temperature (AIT) was taken as the limiting temperature above which a hot surface might ignite a gas mixture. Codes for hazardous area classification have tended to quote AITs as hot surface temperature limits.

It has long been appreciated, however, that there is a difference between the hot surface temperature which will ignite a flammable gas–air mixture and the AIT. This temperature excess depends on the conditions. Relevant factors include the fuel and fuel concentration, the material, area and geometry of the surface, and the fluid flow and heat transfer conditions.

Hot surface ignition has been the subject of a good deal of work and details are given in Section 16.3. This work consistently shows that an appreciable temperature excess is necessary for ignition to occur. It also demonstrates that the temperature excess required increases as the hot surface area decreases. The necessary temperature excess also increases as the gas velocity increases. One effect of increasing the gas velocity is to reduce the residence time of the gas and this may then fall below the ignition induction period.

Industrially oriented work by Husa and Runes (1963) indicated that for hot surfaces in the open air a temperature excess of several hundred degrees was required to give ignition. The systems investigated

Table 16.24 *Some ignition sources on process plants*

A General	
Flames	Flare: elevated or ground level flare; full flare or pilot condition; incinerator
	Furnace: natural or forced draught furnace
	Fired heater
	Boiler
	Laboratory heater: bunsen burner; furnace
	Personnel heater: solid fuel or electrical fire
	Burning operations: burning rubbish; burning during demolition
	Firing: explosion for demolition; other explosives
	Warning flare: hazard warning flare; fog warning detonator
	Accidental fire
	Hot material: brand; hot particles
Hot work	Welding: arc welding; oxyacetylene welding
	Cutting: oxyacetylene cutting
	Grinding
	Hot tapping
Hot surface	General: vessel and pipework
	Machinery: engines; turbines; exhausts
	Laboratory equipment: hot plate; oven
	Hot particles: soot
Friction and impact	Impact: hand tool; power tool; boot stud; loosening of caked material; moving vehicle
	Rubbing: belt, conveyor, roller; brake, clutch on machinery; skidding of road or rail tanker
Hot material or gas	Discharged material: hot ash from boiler; used catalyst; hot process material
	Hot gas
Pyrophoric, reactive and unstable materials	
Engines	Ingestion of flammable: petrol, diesel or gas engine mixture
Chemical effects	Friction and impact: thermite reaction (see above)
	Instrument: catalytic element
Smoking	Means of lighting: matches; lighter
	Item smoked: cigarette; cigar; pipe
Vehicles	General vehicles: petrol, diesel or electrically driven
	Crane
	Forklift truck
	Helicopter
	Aircraft
Atmospherics	Lightning
Radio frequency transmission	See Section 16.5.12
Arson, sabotage	Fire
	Explosion
Compression	Ingestion of flammable mixture: compressor; high speed blower
Mechanical rupture	Spark associated with rupture giving rise to release
Self-heating	Dust layer
	Oil soaked lagging
	See also Section 16.6
Static electricity	See Section 16.7
Electrical	Machinery: motors, alternators, dynamos, converters
	Fixed equipment: contact devices such as switches, relays, contactors
	Fixed equipment – failures: failure of protective equipment; failure causing arcing
	Insulator: arcing across spark gaps at high voltage insulators
	Wiring: loose connection; poor joint; damaged wiring
	Cable: broken cable; damaged cable; water ingress
	Batteries: connecting up damaged battery
	Instrument
	Heating tape
	Lighting
	Fault current conductor: poor joint
	Portable equipment: meter; radio; TV; camera; hearing aid
	Earth movement: sparking due to earth movement such as earthquake or subsidence

B Internal	
Auto-ignition[a]	
Compression	Pump: compression by pumping against closed valve
	Hammer blow: compression by hammer blow in pipeline
	Liquid slug: compression by liquid slug
	Air bubbles: compression of air bubbles in liquid
Reactive, unstable material	Pyrophoric material
	Incompatible material: material which reacts with material of construction
Catalytic material	
Hot material	Hot catalyst; hot dust; hot gas
Hot surface	External hot work
	Rotating machinery: ingestion of tramp metal
	Distressed machinery: hot bearings; hot particles
	Lamp: damaged wander lamp
Electrical	Heater – failure: failure causing overheating
Self-heating	See Section 16.6
Static electricity	See Section 16.7

[a] A flammable mixture can undergo a combustion reaction outside the normal flammability limits. These limits apply essentially to propagation rather than ignition as such.

were, however, not well defined by the standards of more recent work.

Practical guidance is given in API Publ. 2216: 1991 *Ignition Risk of Hydrocarbon Vapors by Hot Surfaces in Open Air*. This draws attention to the work of Hilado and Clark (1972b) and Goodall and Ingle (1967) on the effects on ignition of the induction time and of gas velocity, respectively, and the work of Husa and Runes. It states that as a rule of thumb, and based on open air tests, ignition by a hot surface should not be assumed unless the surface temperature is at least 200°C above the normally accepted minimum ignition temperature.

A hot surface is a potential ignition source inside as well as outside the plant. The rule of thumb just quoted is not intended to apply in this case, although induction time and gas velocity are again relevant factors.

16.5.4 Hot particles

Another form of hot surface is a hot particle. A hot particle which is common on plant is soot from burners or from a flare. Hot soot from chimneys may be a source of ignition. It is a particularly important potential source of ignition on ships.

16.5.5 Friction and impact

Impact, friction and frictional impact can be a source of ignition for a flammable gas–air mixture. A review has been given by F. Powell (1969). An account of some of the fundamental phenomena is given in Section 16.3.

Essentially, incendive sparks caused by impact and friction are due to the generation of a surface hot spot. A falling object can give an incendive spark. The temperature rise may correlate only weakly with the kinetic energy but can be sufficient to cause ignition. It is normal to adopt procedures to prevent damage to the plant by falling objects. However, dropping of objects can occur which may not be controlled by these measures such as drums, hand tools, etc.

Ignition by a falling object is likely to be most serious in a space which already contains a flammable atmosphere. Objects such as tank washing machines or cathodic protection anodes in ships' cargo tanks illustrate this. Cigarette lighter flints can also cause a mechanical spark if the lighter is dropped.

One situation which is liable to cause ignition in frictional impact is where rusty steel with an aluminium smear is hit by a hard object. Under these conditions the thermite reaction occurs. This reaction, which can reach a temperature of 3000°C, is an effective ignition source. The source of the aluminium may be aluminium paint or the impacting object itself.

Work by Kingman, Coleman and Rogowski (1952) has shown that oil bound paints do not give sparks unless preheated to 150°C. Subject to avoidance of such heating, therefore, such paints may be used on steel in hazardous areas.

The striking of quartzitic materials, including concrete containing sand, by a metal tool is another situation liable to give incendive sparks. A report by the Department of Scientific and Industrial Research (DSIR), (1963) gives details of fires attributed to frictional sparks, most of which involved various metals and concrete or stone.

An aspect which has received a good deal of attention over the years is the use of 'non-sparking tools'. Materials used in such tools characteristically do not readily oxidize and have high thermal conductivity.

Reviews of the use of non-sparking tools have been given by F. Powell (1969) and Cross and Farrer (1982). Essentially, some investigators have concluded that regular steel tools are no more hazardous than non-sparking tools, whilst others believe there is a benefit to safety in the use of non-sparking tools. Anfenger and Johnson (1941) performed experiments on the incendivity of sparks produced by steel on a grinding wheel which ignited carbon disulphide but not petrol vapour.

On the basis of this work and practical experience the American Petroleum Institute (API) in *Sparks from Hand Tools* (1956) concluded that there is no significant increase in safety from the use of non-sparking tools. API Publ. 2214: 1989 *Spark Ignition Properties of Hand Tools* states that nothing essentially new has been learned since the 1956 publication and that the fire records of more and more companies which have never used, or have ceased to use, non-sparking tools amply confirm the position then taken. Non-sparking hand tools are discussed further in Chapter 21.

Other workers such as those at the DSIR (1963) and Riddlestone and Bartels (1965) draw attention to ignitions caused by the striking of metals on concrete or stone and point out that it is in this situation that the ignition risk is significant, and that metals used in non-sparking tools are also liable to give ignition in this case. For this rather different reason they conclude that non-sparking tools offer little benefit.

Another point which detracts from the potential benefit of non-sparking tools is that they tend to be soft, so that hard particles can become embedded in the tool.

Other workers have seen a benefit in the use of non-sparking tools. On the basis of impact and grinding experiments Fischer (1965) recommends the use of steel tools for work where there may be Class I gases but not where there may be Class II gases.

Certain gases such as hydrogen, acetylene and carbon disulphide are particularly sensitive to ignition by impact and friction. If such a gas is present there is a potential ignition risk in the use of any tool. Non-sparking tools are considered further in Chapter 21.

A study of ignitions by impact, friction and frictional impact has been made by Billinge (1981). He classifies these ignitions as due to impact, rubbing, or cutting and grinding, and as high, medium or low energy. The individual incidents are shown in Table 16.25 and the analysis of these incidents is given in Table 16.26.

16.5.6 Chemical energy

There are several forms of chemical energy which may give ignition. They include (1) the thermite reaction, (2) reactive, unstable and pyrophoric materials and (3) catalytic instruments. The thermite reaction is obtained from aluminium smears on rusty steel, as described above. Reactive, unstable and pyrophoris materials are considered below.

Some instruments contain catalytic elements which measure the temperature rise resulting from combustion of a flammable gas. Generally, these instruments, such as flammable gas detectors, are intended to operate in hazardous areas and are therefore designed so that they should not act as an ignition source.

Table 16.25 *Some incidents involving friction and impact ignition relevant to the process industries in the period 1958–78 (after Billinge, 1981): details of incidents (Courtesy of Fire Prevention Science and Technology)*

A Gases and vapours

Fuel	*Cause*	*Classification*
Group IIA		
Petrol	Spark from hammer; hammer on steel clasp; shoe nail on concrete floor; boot nail on concrete floor; dropped tool or steel tipped boot on concrete floor; dropped tool on floor; screwdriver punched through drum lid	Low energy impact
	Falling drum; dropped can of petrol on floor; impact between drums; impact between car and petrol pump; impact between cars	Medium energy
	Sparking from brakes of rail tank wagon	Medium energy rubbing
	Collision between ships	High energy impact
	Skidding overturned road tanker (×3); barge ripped open by bridge fender	High energy rubbing
Jet fuel	Tanker scraped lock wall	
Crude oil vapour	Magnesium anode impact; pipeline coupling falling onto ship's deck	Medium energy impact
	Collision between ships	High energy impact
Oil vapour	Defective pump	Medium energy rubbing
	Ferrous metal in aluminium polishing and grinding machine	Medium energy cutting and grinding
LPG	Steel cylinders with aluminium smears	Low energy impact
	Crashing rail wagons	High energy impact
Liquefied butane	Crashing road tanker	High energy impact
Propane	Valve knocked off gas tank	Medium energy impact
	Impact of aluminium wrench on pipe joint	Low energy impact
Pentane	Metal object in chopping machine	Medium energy impact
Benzene	Collapsing metalwork	Medium energy impact
Natural gas	Tool dropped down oil well	Medium energy impact
	Mechanical shovel fractured gas main	High energy impact
Methanol	Impact between nozzle and wall	Medium energy impact
	Tramp metal in grinding process	Medium energy cutting and grinding
	Belt rubbing on copper tube	Medium energy rubbing
Ethanol	Friction in centrifuge	Medium energy rubbing
	Impact between digger and centre cone of centrifuge	Medium energy impact
	Grindstone sparks	Medium energy cutting and grinding
Hexane/ethanol	Friction in centrifuge	Medium energy rubbing
Isopropanol	Impact of drum on ground	Medium energy impact
Acetone	Impact of drum on ground	Medium energy impact
Acrylic paint solvent	Defective extractor motor fan	Medium energy rubbing
Mixed solvent vapours	Truck ran over drum of solvent	Medium energy rubbing
	Impact between drum or lighter and floor	Medium energy impact

Table 16.25 *(Continued)*

A - continued

Fuel	*Cause*	*Classification*
Ethyl chloride	Impact between metal ditch covers	Medium energy impact
Vinyl acetate	Impact between filling nozzle and loading aperture	Medium energy impact
Group IIB		
Ethylene	Unscrewing valve from pipe	Low energy impact
	Sparks from bursting tyre	Medium energy cutting and grinding
Coke oven gas	Collapsing shelf holding gas meter	Medium energy impact
Group IIC		
Hydrogen	Hammer hitting bolts on steam line; spark between cylinder cap and tool	Low energy impact
	Drilling pipe; abrasive cutting and grinding of pipe	Medium energy cutting and grinding
Acetylene	Moving or opening drum of carbide; cylinder fell from lorry; feed cone dropped into hopper of carbide	Medium energy impact
	Sparks from grinding process	Medium energy cutting and grinding
Carbon disulphide	Impact between brass rod and caked material	Low energy impact
Various vapours and solvents	Gear wheels not properly meshed; friction in centrifuge; falling metalwork; dismantling metalwork; agitator fell into mixing tank	Medium energy impact
	Cellulose film rubbing on roller	Medium energy rubbing
	Cutting pipe with (mechanical) hacksaw	Medium energy cutting and grinding
B Powders and dusts		
Foodstuffs		
Grain dust	Nut, bolt or stone in suction pipe; metal object in hopper machine	Low energy impact
	Impact of pulley with wall; foreign body in mill	Medium energy impact
Sugar dust	Wood screw fell into mill	Medium energy impact
	Elevator buckets rubbing on guides	Medium energy rubbing
Peppercorn dust	Foreign body in mill	Medium energy impact
Flour dust	Overheated bearing (×3); overheated motor	Medium energy rubbing
Flour and grain dust	Overheated pulley and belt drive	Medium energy rubbing
Corn dust	Friction between belt drive and pulley guard	Medium energy rubbing
Organic chemicals		
Organic powder	Foreign body in mill	Medium energy impact
Niacin dust	Bolt in mill	Medium energy impact
Phenolic moulding powder	Spark from unknown agent	Medium energy impact
	Spark from grinding machine	Medium energy cutting and grinding
Cellulose nitrate dust	Chipping concrete with air hammer	Medium energy impact
Dinitrosopentamethylene tetramine	Impact of fork lift truck with fibre container	Medium energy impact
Diazonium salt	Hammering wedges	Low energy impact
Sodium picramate	Impact of drum on floor	Medium energy impact

Inorganic chemicals		
Giant gel 40% dope/sulphur	Aluminium tamp punch on steel grating bars	Low energy impact
Ammonium perchlorate	Scraping with spatula	Low energy impact
	Spatula left in mixer	Medium energy rubbing
	Friction from beryllium cutting knives	Medium energy cutting and grinding
Thermite	Cleaning edge runner mill	Low energy impact
Aluminium powder	Steel tool on rusty lid of container	Low energy impact
Sulphur	Mechanical shovel striking metal deck; mechanical impact of crane grab with bulkhead; metal grabs striking ships structure; frictional spark from crane grab; mechanical shovel hitting side of ship's hold; steel tub falling into ship's hold	Medium energy impact
Windproof matches	Carton of matches fell 2 m	Medium energy impact
Rocket propellant	Metal–metal contact in mixer	Medium energy rubbing
Pyrotechnic mixture	Metal–metal contact in mixer	Medium energy rubbing
Zirconium dust	Sparks from grinding steel	Medium energy cutting and grinding
Powder	Hopper fell and impacted tram car	Medium energy impact
Oil mist	Overheated pump	Medium energy rubbing

Table 16.26 *Some incidents involving friction and impact ignition relevant to the process industries in the period 1958–78 (after Billinge, 1981): analysis of incidents (Courtesy of Fire Prevention Science and Technology)*

	No. of incidents	
	Gases and vapours	*Powders and dusts*
Low energy: impact	13	7
Medium energy:		
impact	27	19
rubbing	8	11
cutting and grinding	8	3
High energy:		
impact	5	–
rubbing	5	–
Total low energy	13	7
Total medium energy	43	33
Total high energy	10	–
Total impact	45	26
Total rubbing	13	11
Total cutting and grinding	8	3
Overall total	66	40

16.5.7 Hot materials and gases

Hot materials such as hot ash, hot used catalyst or hot process material, and hot gases may, in principle, act as ignition sources. Generally, however, operations involving such hot materials are excluded from hazardous areas and they do not figure as a significant ignition source.

16.5.8 Reactive, unstable and pyrophoric materials

Reactive, unstable or pyrophoric materials may act as an ignition source by undergoing an exothermic reaction so that they become hot. In some cases the material requires air for this reaction to take place, in others it does not.

The most commonly mentioned pyrophoric material is pyrophoric iron sulphide. This is formed from reaction of hydrogen sulphide in crude oil in steel equipment. If conditions are dry and warm, the scale may glow red and act as a source of ignition. Pyrophoric iron sulphide should be damped down and removed from the equipment. No attempt should be made to scrape it away before it has been dampened.

A reactive, unstable or pyrophoric material is a potential ignition source inside as well as outside the plant.

16.5.9 Engines

Engines on process plants are another ignition source and tend to figure significantly.

One type of engine in use for a variety of purposes is the diesel engine. Guidance on the use of diesel engines in relation to hazardous areas is given in a number of codes. One is *Guidelines on Protection of Diesel Engines for Hazardous Zone 2 Areas* (Lloyd's Register, n.d.). Another is *Recommendation for the Protection of Diesel Engines Operation in Hazardous Areas* (Oil Companies Materials Association, 1977).

A discussion of diesel engines in this context has been given by Sokolov (1989), who considers the various potential ignition sources on the engine and the steps which can be taken to prevent ignition by these sources.

One potential ignition source on a diesel engine is the hot gas. Exhaust gas temperatures can be as high as 500°C. Ignition by hot exhaust gas involves turbulent stream ignition, which can occur at a temperature less than the average temperature of the gas mixture. A

safety factor is therefore required. Codes typically recommend that the temperature of the exhaust gas should not exceed 0.6–0.8 of the AIT of any flammable gas which may be present. Sokolov quotes the following:

Gas	*Ignition temperature* (°C)	*Safe exhaust gas temperature* (°C)
Methane	595	396
Propane	470	313
Natural gas	482–650	320
Condensate	275	183

Another important part of the engine is the induction and exhaust systems. These systems are designed to avoid detonation but to handle deflagration. There are minimum design pressures which tend to lie in the range 8–10 bar, that for the UK being 10 bar and that for the USA 8.6 bar. Induction and exhaust systems are provided with flame arresters; exhausts are provided with spark arresters.

Crank cases are another feature of a diesel engine which requires protection.

The preferred start-up arrangements for the engine in a hazardous area are pneumatic, hydraulic or manual rather than electrical.

Diesel engines are generally equipped with shut-down devices and alarms activated by overspeed and by failures of the various subsystems. Depending on the application, the device may act to cut off the fuel or to shut off the air intake and effect gradual gas path deflection.

16.5.10 Vehicles

A chemical works may contain at any given time considerable numbers of vehicles. These vehicles are potential sources of ignition. Instances have occurred in which vehicles have had their fuel supply switched off, but have continued to run by drawing in, as fuel, flammable gas from an enveloping gas cloud. The ignition source of the flammable vapour cloud in the Feyzin disaster in 1966 was identified as a car passing on a nearby road (Case History A38). It is necessary, therefore, to exclude ordinary vehicles from hazardous areas and to ensure that those which are allowed in cannot constitute a ignition source.

Vehicles which are required for use on process plant include cranes and forklift trucks. Various methods have been devised to render vehicles safe for use in hazardous areas and these are covered in the relevant codes.

16.5.11 Lightning

Lightning is another potential ignition source on process plants. Information on lightning and on lightning protection is given in *Lightning* (Golde, 1977a).

Lightning has traditionally been a significant ignition source for storage tank fires. A major incident of this kind occurred at Beaumont, Texas, in 1970 (Case History A46).

Guidance on lightning protection is given in BS 6651: 1985 *Code of Practice for Protection of Structures against Lightning.*

16.5.12 Radio frequency transmissions

The possibility exists that radio frequency (RF) transmissions from strong sources such as large military transmitters may act as an ignition source on process plants. This has been recognized for some time as instanced by the existence of a British Standard BS 4992: 1974 *Guide to Protection Against Ignition and Detonation Initiated by Radio Frequency.*

A situation where concern was expressed about such possible interaction arose in Britain in the late 1970s in respect of the transmitter at Crimond operated by the Royal Navy and located about 4 miles from the natural gas terminal at St Fergus. The naval transmitter responded by reducing its power output.

Studies of this hazard were undertaken by a number of workers (A. Hall and Burstow, 1980; A. Hall and Loveland, 1980; Burstow *et al.*, 1981; Howson, Excell and Butcher, 1981; Rosenfeld *et al.*, 1981) and the Health and Safety Executive (HSE) published two reports*: Assessment of the Hazard from Radio Frequency Ignition at the Shell and Esso Sites at Braefoot Bay and Moss Morran, Fife* (HSE, 1978a) and *Report of the Steering Committee on Radio Frequency Ignition Hazards at St Fergus, Scotland* (HSE, 1979f).

The British Standard guidance was revised and issued as BS 6656: 1986 *Prevention of Inadvertent Ignition of Flammable Atmospheres by Radio-frequency Ignition*, and revised again in 1991.

The conditions for RF ignition of a flammable mixture to occur are (1) electromagnetic radiation of sufficient intensity, (2) a structure capable of acting as a receiving aerial and (3) a mechanism for creating an incendive spark.

The transmitter may be fixed or mobile. Mobile transmitters include vehicles, ships and aircraft. The standard give details of typical transmitter frequency ranges and power outputs. Transmission may be continuous wave (CW) or modulated. The latter includes pulsed radar.

The degree of hazard depends on the frequency of the transmission. The hazardous range of interest is 15 kHz to 35 GHz. There is little hazard at frequencies below 15 kHz. For frequencies below 30 MHz the most efficient receiver is the loop configuration. At higher frequencies all structures are large compared with the wavelength. A part of a structure may behave as an efficient aerial and is then treated as a long dipole. An aerial can concentrate the power in a particular direction and is said to have gain in that direction.

The structures primarily considered in BS 6656: 1991 are loop-type structures and vertical structures. Some typical loop-type structures are illustrated in Figure 16.34. A loop structure has maximum efficiency and is self-resonant when its internal perimeter is about half one wavelength, but structures with a smaller perimeter can be brought to resonance if there is a discontinuity with stray capacitance across it. Cranes are particularly efficient receivers in this context and require particular attention.

For any potential discontinuity in the structure it is possible to determine the maximum extractable power given (1) the structure perimeter, (2) the transmission frequency and (3) the incident field strength.

Vertical structures include vents, flares and columns. Free-standing structures of this kind are not classed as

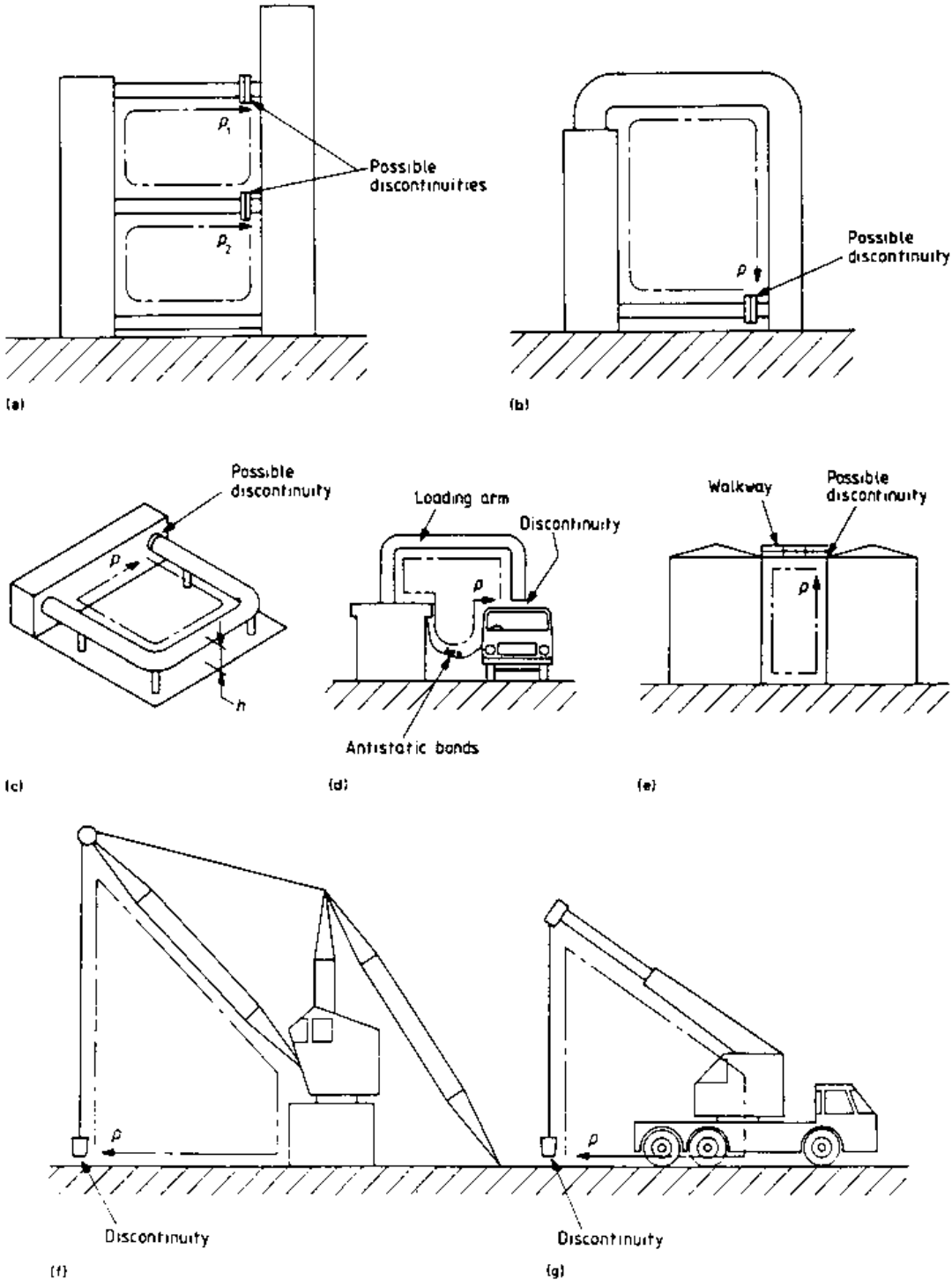


Figure 16.34 *Some typical loop-type structures for RF ignition (BS 6656: 1991): (a) loop formed by columns and pipes; (b) loop formed by columns and pipes; (c) horizontal loop; (d) tanker loading facility; (e) storage tanks; (f) fixed crane; and (g) mobile crane. h, Height of loops; p, internal perimeter of loop (Courtesy of the British Standards Institution)*

Table 16.27 *Maximum radius of search area* (m) *for initial assessment of an RF ignition hazard*[a] *(BS 6656: 1991) (Courtesy of the British Standards Institution)*

Gas group	*Maximum radius* (m)	
	All loop structures of inside perimeter ≤ 40 *m and horizontal loops of height* ≤ 5 *m*	*All other loop structures*
I or IIA	4100	11 500
IIB	5200	14 200
IIC	6500	17 500

[a]Table does not apply to locations to the seaward side of Orford Ness, Suffolk.

among the more efficient receivers, since even a concrete base has a low impedance path to earth. They can generally be disregarded, except where the vertical structure is part of a loop.

An RF discharge occurs most readily when two surfaces are drawn apart, thus giving a break-spark. Discharges across a fixed gap are not considered to be a significant problem. It is activities such as maintenance and handling and phenomena such as flexing and vibration of pipework or thermal expansion of structures which are liable to give rise to an incendive discharge.

The factor determining RF ignition is the thermal initiation time. For times less than this ignition is governed by the discharge energy, and for times greater than this it is governed by its power. The thermal initiation times are approximately 100 μs for methane and ethylene and 20 μs for hydrogen, which are representative of the Class IIA, IIB and IIC gases, respectively. The standard gives ignition criteria for continuous transmissions and for pulsed radar transmissions.

The potential RF ignition hazard exists only in a few locations. There are few reported incidents of such ignition. BS 6656: 1991 adopts a graded approach to assessment of the hazard. An initial assessment is used for screening and a full assessment is undertaken only if a potential hazard is found to exist.

The initial assessment is based on the search areas given in Table 16.27 and proceeds as follows. The search area around the plant is determined from the table. If there is no transmitter within the search area, there is no hazard. If there is a transmitter with the search area, a check is made as to whether the plant is within the vulnerable zone of the transmitter. The standard gives information on the vulnerable zones for various types of transmitter. If the plant is within the vulnerable zone of a transmitter, a full assessment should be undertaken.

BS 6656: 1991 gives the procedures for a full assessment, including: a flow chart for a theoretical assessment and one for an assessment based on plant measurements; methods of taking measurements; methods of performing the calculations; and worked examples.

If a hazard exists, the principal countermeasures are (1) bonding, (2) insulating, (3) reducing the RF efficiency of structures and (4) de-tuning of structures. Typical applications where bonding might be used are where thermal expansion may result in intermittent contacts and across a pair of flanges prior to their parting in maintenance work. Bonding to earth is not suitable. Insulation may sometimes be used where bonding is impractical; it is a possible solution for intermittent contact by thermal expansion. The RF efficiency of a structure may be reduced at the design stage by altering the internal perimeter. Other measures for reducing efficiency include breaking the loop into smaller sections by the use of conductors and covering the entire area of the loop with a sheet of metallic mesh bonded to the structure at points around the perimeter. If there is one major transmission frequency causing the problem and other measures are not practical, it may be possible to detune the structure by connecting to it reactive components.

Special cases considered in the standard include cranes, mobile and portable transmitters, ships and offshore platforms. The Orford Ness transmitter is accorded special treatment.

16.5.13 Smoking

Smoking and smoking materials are potential sources of ignition. Ignition may be caused by a cigarette, cigar or pipe or by the matches or lighter used to light it. A cigarette itself may not be hot enough to ignite a flammable gas–air mixture, but a match is a more effective ignition source.

It is normal to prohibit smoking in a hazardous area and to require that matches or lighters be given up on entry to that area. The 'no smoking' rule may well be disregarded, however, if no alternative arrangements for smoking are provided. It is regarded as desirable, therefore, to provide a room where it is safe to smoke, though whether this is done is likely to depend increasingly on general company policy with regard to smoking.

16.5.14 Arson and sabotage

A source of ignition which cannot be ruled out is arson. Information on the frequency of arson as a source of ignition was given in Table 2.11. While arson is probably a less important cause of fires in the process industry than of fires generally, it should nevertheless be considered. Security in relation to arson is discussed in Chapter 20.

16.5.15 Autoignition

Strictly, ignition of a bulk flammable gas–air mixture by heating the mixture to its autoignition temperature is the alternative to ignition by a local ignition source. It is convenient, however, to deal with it at this point.

Heating of the bulk gas–air mixture outside the plant will occur by contact with a hot surface, as described above. Autoignition as such may therefore be regarded as a form of ignition which occurs inside the plant.

The autoignition may occur inside the plant at essentially atmospheric pressure or at some higher pressure. If, however, the heating occurs due to

compression, the phenomenon is one of compression ignition, which is described blow.

16.5.16 Compression effects

A mixture of flammable gas and air may be heated to its autoignition temperature by compression. This effect is often referred to as the diesel effect. There are a number of conditions in process plant which can give rise to such compression.

Compression ignition is described in Section 16.3. The point was made there that, given a homogeneous mixture, such autoignition is not restricted to the normal flammability range.

Compression of a mixture of flammable gas and air may be caused by pumping against a closed valve, by water hammer in a pipeline or by a liquid slug travelling down a line.

A case history involving compression ignition in which a mixture of flammable gas and air was compressed by a pump pumping against a closed valve is described by Anon. (LPB 19 1978, p. 24). The pump had a nominal head of 30 m. Subsequent tests showed that pressure oscillations occurred in the trapped gas which were up to 8 times higher than the equilibrium head of the pump.

Another form of compression ignition can occur due to compression of air bubbles in a flammable liquid. The temperature rise inside such bubbles can be high.

16.6 Self-heating

Self-heating, or spontaneous combustion, of a solid material is generally a process of slow oxidation. Material undergoing self-heating may act as a source of ignition or it may give rise to a fire or explosion. The topic of thermal explosion and self-heating has many ramifications beyond the self-heating of solid materials. These other aspects are considered in Section 16.3.

Early work on self-heating was done by Frank-Kamenetsky (1955) and by Semenov (1935). P.H. Thomas and Bowes, both separately and together, have published a series of treatments (e.g. P.H. Thomas, 1958; P.H. Thomas and Bowes, 1961a, 1967; Bowes, 1976). The subject has been reviewed in *Self-heating* (Bowes, 1984) and by P. Gray and Lee (1967b). Application of the theory to process plant problems has been discussed by Bowes (1976).

Selected references on self-heating are given in Table 16.28.

16.6.1 Self-heating in industrial processes

Materials in process, storage or transport may undergo self-heating. The self-heating is due to the exothermic reaction of slow oxidation of the material. If conditions are critical, this self-heating results in ignition. Examples are materials handled in process equipment such as driers, materials stored in piles in warehouses or in the open, or materials transported in large containers as in ships. A well known example is the spontaneous combustion of coal stored in piles on the ground.

In some cases the hazard is intensified by the fact that the material enters the storage relatively hot. This can occur, for example, with material which has just been passed through a drier.

Unstable materials may also undergo an exothermic reaction so that self-heating occurs.

Table 16.28 *Selected references on thermal explosion, self-heating and spontaneous combustion*

Mackey (1895, 1896); Semenov (1928, 1935, 1940, 1942, 1959); Frank-Kamenetsky (1939a,b, 1942, 1945, 1955); Zeldovitch (1939); Gordon (1948); Rideal and Robertson (1948); N.D.Mitchell (1951); A. Thomas (1951); Chambré (1952); Bowes (1954, 1962, 1968, 1969, 1972, 1974a,b, 1976, 1984); Hicks (1954); Mullins (1955); Enig (1956, 1966); Enig, Shanks and Southworth (1956); Khitrin and Goldenberg (1957); P.H. Thomas (1958, 1960, 1961, 1965a, 1972, 1973a, 1984); Cook (1959); P. Gray and Harper (1959a,b); Kinabara and Akita (1960); Zinn and Mader (1960); Parks (1961); P.H. Thomas and Bowes (1961a,b, 1967); Bowes and Townshend (1962); Gross and Amster (1962); Zinn (1962); Boddington (1963); M.H. Friedman (1963a,b, 1967, 1968); Merzhanov, Barzykin and Gontovskaya (1963); Adler and Enig (1964); Wake and Walker (1964); Clemmow and Huffington (1965); P. Gray and Lee (1965, 1967a,b); Steggerda (1965); Bowes and Thomas (1966); van Geel (1966); Merzhanov (1966, 1967); Merzhanov and Dubovitsky (1966); B.F. Gray and Yang (1967); Gugan (1967, 1974a); Tyler and Wesley (1967); Bowes and Langford (1968); B.F. Gray (1969a,b, 1973–); P. Gray, Lee and MacDonald (1969); Rosser and Rajapakse (1969); Boddington and Gray (1970); Boddington, Gray and Harvey (1971a,b); Merzhanov and Averson (1971); Wake (1971, 1973); Birkby, Brown and Street (1972); FRS (1972 Fire Res. Note 937); Goodman, Gray and Jones (1972); B.F. Gray and Sherrington (1972); Hardee, Lee and Donaldson (1972); Hermance (1973); Wake and Rayner (1973); Shouman, Donaldson and Tsao (1974); Zaturska (1974, 1975, 1978, 1980, 1981, 1983, 1984); Kassoy and Poland (1975); Shouman and Donaldson (1975, 1977); MacDermott (1976); P. Gray and Sherrington (1977); Kerns (1977 BM IC 8757); Takeno (1977); Adler (1978, 1983, 1987); BRE (1978 CP12/78, 1982 IP6/82, 1984 SO 41); Anthony and Greaney (1979); Boddington, Gray and Robinson (1979); Gill, Donaldson and Shouman (1979–); Kordylewski (1979, 1980); Naujokas (1979, 1985); Brogli (1980); Brogli *et al.* (1980); Drysdale (1980); Takemo and Sato (1980); M.M. Baum (1981); Beever (1981); Boddington, Gray and Scott (1981); Gill, Shouman and Donaldson (1981); B.F. Gray and Jones (1981); Kordylewski and Krajewski (1981, 1985); Lawn, Street and Baum (1981); Tyler and Jones (1981); Boddington, Chang-Gen Feng and Gray (1982); Egeiban *et al.* (1982); Poland, Hindash and Kassoy (1982); Zaturska and Banks (1982, 1990); Adler and Bowes (1983); B.F. Gray and Wake (1984, 1988); Lermant and Yip (1984–); Vega and Linan (1984); Gomez, Wake and Gray (1985); B.F. Gray and Scott (1985); Greenway and Spence (1985); Griffiths, Hasko and Tong (1985); Winters and Cliffe (1985); Adler (1987); Snee 1987, 1989); Brooks, Balakotaiah and Luss (1988); Ahmed, Fisher and Janeshek (1989); de Faveri, Zonato *et al.* (1989); P. Gray and Griffiths (1989); Kassoy, Kapila and Stewart (1989); Kotoyori (1989a, 1993); Babushok, Goldshtein and Sobolev (1990); Benin, Kossoi and Sharikov (1990); McIntosh and Tolputt (1990); Britton (1991); Gorelov and Sobolev (1991); J.F. Griffiths and Kordylewski (1992a,b); Schliephake, Giesbrecht and Loffler (1992); Uehara and Seino (1992); Davie, Nolan and Tucker (1993); H. Martin and Ruppert (1993); Vaughan and Mancini (1993); El-Sayed (1994)

Self-heating is liable to occur in oil-soaked lagging. In this case it is the oil which undergoes oxidation. Self-heating may also occur in dust layers. In both cases the smouldering material may then act as an ignition source.

Self-heating can also occur in oil rags left on steam pipes, in dirty cotton waste put in a boiler suit pocket, or in damp clothing stowed away in a locker.

The substance which undergoes reaction must be reactive and may be bulk solid such as coal or a reactive substance on a substrate such as oil-soaked lagging.

16.6.2 Self-heating incidents

Most incidents due to self-heating arise in the kind of situations just described. Usually they do not have dramatic consequences. This is not always so, however.

In 1987, a severe explosion and fireball occurred at the BP Chemicals ethylene oxide (EO) plant at Antwerp (Case History A115). The cause of the explosion was identified as the decomposition of EO in the purification column. It was concluded that the most probable cause of the explosion was a leak of EO into the insulation of the column, leading to self-heating which ignited the escaping EO.

In 1989, the BASF ethylene oxide plant at Antwerp suffered two severe explosions, each accompanied by a fireball (Case History A122). The first explosion occurred in a column separating EO and acetaldehyde. The investigation found that a small leak of EO had probably led to an accumulation of auto-oxidizable polyethylene glycols in the insulation of the column. Self-heating occurred in the insulation. Although the heat released would not have been enough to cause decomposition of the EO flowing past on the inside of the column, it was concluded that decomposition occurred at a section of pipework where the gas was stagnant.

16.6.3 Self-heating process

If self-heating occurs, the occurrence of a thermal explosion depends on the heat balance in the solid. The heat balance is illustrated in Figure 16.35 (after Semenov). The rate of heat release is a function of the temperature as shown in curve A. Over the lower temperature range the reaction is rate limited and the reaction rate, and hence the heat released, rises rapidly. The rise is often governed by an exponential relation, and in particular by the Arrhenius equation. Over the higher temperature range the rate becomes diffusion limited and increases only weakly with temperature, so that the reaction rate and the heat released then increase relatively slowly.

The heat removed is approximately proportional to the temperature difference between the solid mass, or pile, and the surrounding medium. A series of lines can be drawn corresponding to different effective heat transfer coefficients. Line B1 is tangential to curve A at point 1. For the condition where the heat transfer is greater than this, the heat removed will always be greater than heat released and no thermal explosion will occur. Line B3 is tangential to curve A at point 5. For any condition where heat transfer is less than this, the heat removed will always be less than the heat released and thermal explosion will occur. Line B2 represents the intermediate case. It crosses curve A at the three points 2, 3 and 4, which each constitute a steady state. Points 2 and 4 are

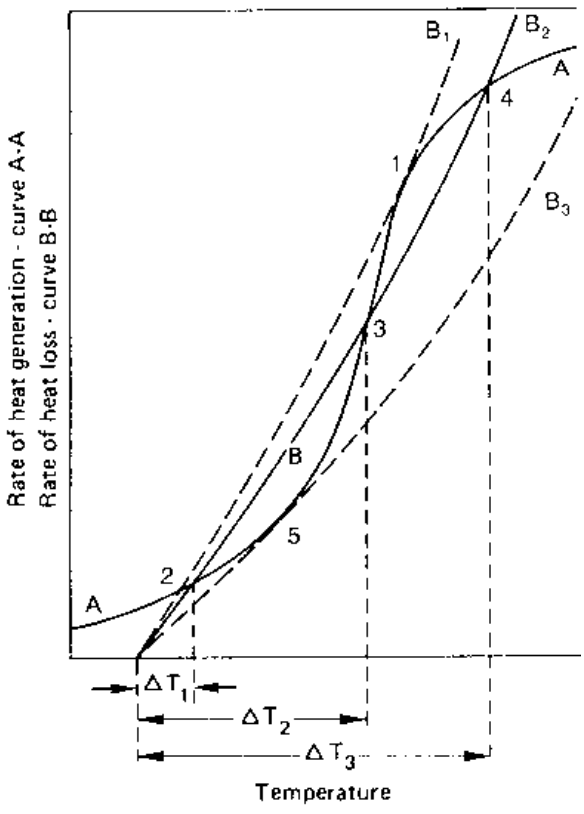


Figure 16.35 *Heat balance in a body undergoing self-heating (Bowes, 1984) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

stable steady states in that if there is a small increase in the temperature difference ΔT, the heat removed is greater than that released and the system returns to the steady state point. Point 3, however, is an unstable steady state in that if there is a small increase in ΔT the heat removed is less than that released so that the system will tend move up curve A to the stable steady state at point 4. Conversely, if there is a small decrease in ΔT the system will tend to move down curve A to point 2.

It is also instructive to consider the effect of the size of the solid mass and the temperature difference ΔT between the centre of the mass and the surroundings as shown in Figure 16.36. There are two critical dimensions (r_1 and r_2) and four regions (A–D). There are two curves 1 and 2, which typically correspond to moderate heating and smouldering combustion. If the dimension of the solid mass is less than r_1 and the initial temperature difference is in region A, the temperature difference will move to the value on curve 1 corresponding to the value of r. If the dimension is greater than r_1 and the initial temperature difference is in region B, the temperature difference will move to curve 2. If the dimension lies between r_1 and r_2 and the initial temperature difference is in region B or C, there are two possibilities. If the

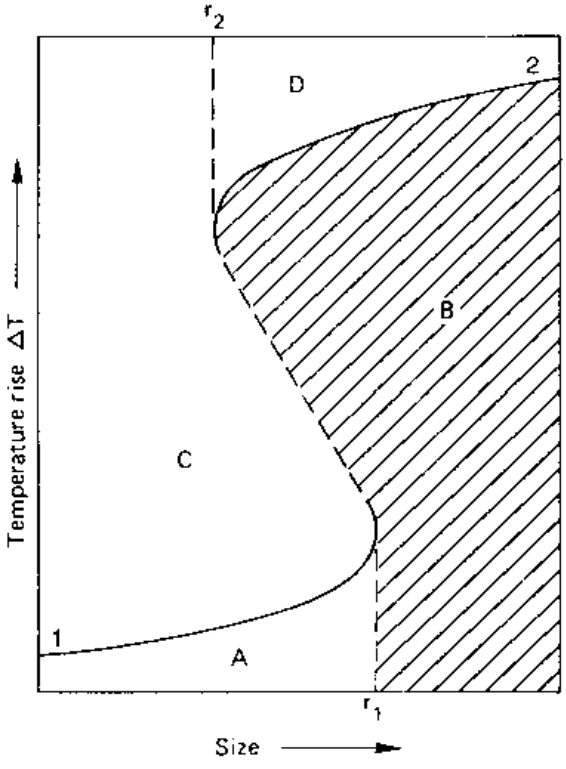


Figure 16.36 *Steady states in a body undergoing self-heating (Bowes, 1984) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

temperature difference tends towards a value within region C, it will move to curve 1. If it tends towards region B, it will move to curve 2. If the dimension lies between r_1 and r_2 and the initial temperature difference is in region A, the temperature difference will move to curve 1, unless an additional heat source shifts it to curve 2. If the dimension is greater than r_2 and the initial temperature difference is in region D, the temperature difference will move to curve 2.

These considerations bring out the importance of the size of the pile. If the size of the pile is small, the system will tend to move towards curve 1, and if the pile is large the system will tend to move toward curve 2.

16.6.4 Elementary relations of self-heating

The basic equation for self-heating is

$$\rho c \frac{\partial T}{\partial t} = k\nabla^2 T + Q \qquad [16.6.1]$$

with

$$Q = Q'\rho A \exp(-E/RT) \qquad [16.6.2]$$

where A is the pre-exponential factor, c is the specific heat, E is the activation energy, k is the thermal conductivity, Q is the heat released by the reaction per unit volume, Q' is the heat of reaction per unit mass, R is the universal gas constant, T is the temperature and ρ is the density.

For the three principal centrisymmetric shapes of interest – the slab, cylinder and sphere – Equation 16.6.1 becomes, in rectangular co-ordinates in one dimension,

$$\rho c \frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{j}{x}\frac{\partial T}{\partial x}\right) + Q'\rho A \exp(-E/RT) \qquad [16.6.3]$$

with

$j = 0$ Plane slab
$j = 1$ Cylinder
$j = 2$ Sphere

where x is the distance from the centre of the body.

The heat transfer at the surface is characterized by an overall heat transfer coefficient h such that

$$-k\frac{\partial T}{\partial t} = h(T_s - T_a) \qquad [16.6.4]$$

with

$$h = h_c + h_r \qquad [16.6.5]$$

where h is the heat transfer coefficient at the surface, h_c is the heat transfer coefficient for convection and h_r is the heat transfer coefficient for radiation.

The following dimensionless quantities are defined. The dimensionless distance z is

$$z = x/r \qquad [16.6.6]$$

where r is the half-width or radius, or characteristic length, and z is the dimensionless distance.

The dimensionless time τ is

$$\tau = \frac{kt}{\rho c r^2} \qquad [16.6.7]$$

The dimensionless parameter ϵ is

$$\epsilon = RT_a/E \qquad [16.6.8]$$

where T_a is the air absolute temperature.

The dimensionless temperature difference θ is

$$\theta = \frac{E}{RT_a^2}(T - T_a) \qquad [16.6.9]$$

The dimensionless ignition parameter δ is

$$\delta = \frac{E}{RT_a^2}\frac{r^2}{k}Q'\rho A \exp(-E/RT_a) \qquad [16.6.10]$$

Frank-Kamenetsky introduced the approximation

$$-\frac{E}{RT} \approx -\frac{E}{RT_a} + \frac{\theta}{1+\epsilon\theta} \qquad E/RT_a \ll 1 \qquad [16.6.11a]$$

$$\approx -\frac{E}{RT_a} + \theta \qquad \epsilon \ll 1 \qquad [16.6.11b]$$

Then, utilizing Equations 16.6.6–16.6.11, Equation 16.6.3 becomes, in dimensionless form,

$$\frac{\partial\theta}{\partial\tau}=\frac{\partial^2\theta}{\partial z^2}+\frac{j}{z}\frac{\partial\theta}{\partial z}+\delta\exp[\theta/(1+\epsilon\theta)] \qquad [16.6.12a]$$

$$\frac{\partial\theta}{\partial\tau}=\frac{\partial^2\theta}{\partial z^2}+\frac{j}{z}\frac{\partial\theta}{\partial z}+\delta\exp\theta \qquad \epsilon\ll 1 \qquad [16.6.12b]$$

and Equation 16.6.4 becomes

$$\frac{\partial\theta}{\partial z}=-\alpha\theta_s \qquad [16.6.13]$$

with

$$\alpha=hr/k \qquad [16.6.14]$$

where α is the Biot number.

Equation 16.6.12 is the basic dimensionless equation of self-heating, as formulated by Frank-Kamenetsky. The parameter δ is the Frank-Kamenetsky parameter.

Use is also made of the following further dimensionless temperature differences:

$$\theta_s=\frac{E}{RT_a^2}(T_s-T_a) \qquad [16.6.15]$$

$$\theta_o=\frac{E}{RT_a^2}(T_o-T_a) \qquad [16.6.16]$$

where subscripts o and s denote the centre of the body and the surface, respectively.

At steady state Equation 16.6.12 becomes

$$\frac{\partial^2\theta}{\partial z^2}+\frac{j}{z}\frac{\partial}{\partial z}=-\delta\exp\theta \qquad [16.6.17]$$

Equation 16.6.17 is the Poisson–Boltzmann equation.

The principal sets of boundary conditions which are used with Equations 16.6.12 and 16.6.17 are:

(1) surface exposed to air – surface heat transfer coefficient finite;
(2) surface exposed to air – surface heat transfer coefficient zero;
(3) surface exposed to air – surface heat transfer coefficient infinite;
(4) one surface against a hot body – constant temperature at hot face;
(5) one surface against a hot body – constant heat flux at hot face.

The second boundary condition is referred to as the Semenov condition and the third as the Frank-Kamenetsky condition.

16.6.5 Model for a symmetrical slab

One principal configuration is the symmetrical slab. For the steady-state condition the temperature profile for self-heating is as shown in Figure 16.37(a). From Equation 16.6.17, setting $j=0$

$$\frac{d^2\theta}{dz^2}=-\delta\exp\theta \qquad [16.6.18]$$

Assuming a finite surface heat transfer coefficient, the boundary conditions are

$$z=0;\ \frac{d\theta}{dz}=0 \qquad [16.6.19a]$$

$$z=\pm 1;\ \frac{d\theta}{dz}=-\alpha\theta_s \qquad [16.6.19b]$$

The general solution of Equation 16.6.18 is

$$\theta=\ln C_2-2\ln\cosh[z(\delta C_2/2)^{\frac{1}{2}}+C_1] \qquad [16.6.20]$$

Differentiating Equation 16.6.20 and utilizing boundary condition 16.6.19a,

$$C_1=0 \qquad [16.6.21a]$$

and

$$C_2=\exp\theta_o \qquad [16.6.21b]$$

Utilizing boundary condition 16.6.19b

$$2D\tanh D=\alpha\theta_s \qquad [16.6.22]$$

with

$$D=\left(\frac{\delta\exp\theta_o}{2}\right)^{\frac{1}{2}} \qquad [16.6.23]$$

Eliminating θ_s from Equations 16.6.20 and 16.6.22

$$\ln\delta=\ln\frac{2D^2}{\cosh^2 D}-2D\frac{\tanh D}{\alpha} \qquad [16.6.24]$$

16.6.6 Characteristics of symmetrical slab model

It is instructive to consider the characteristics of the slab model. For low values of heat transfer at the surface, and hence of α, Equations 16.6.20–16.6.24 imply that

$$\theta_o\to\theta_s \qquad \text{and} \qquad \delta\to 0 \qquad \text{as} \qquad \alpha\to 0$$

From Equations 16.6.22 and 16.6.24

$$\frac{(2\delta)^{\frac{1}{2}}\sinh[(\delta\exp(\theta_o)/2)^{\frac{1}{2}}]}{\alpha}=\theta_s\exp(-\theta_s/2) \qquad [16.6.25]$$

In the region $0<\alpha<1$, $0<\delta<1$, $\theta_o\approx\theta_s$, Equation 16.6.25 reduces to

$$\delta/\alpha=\theta_s\exp(-\theta_s) \qquad [16.6.26]$$

Equation 16.6.26 implies that for a given value of α the parameter δ passes through a maximum with θ_s and has this maximum at $\theta_s=1$. This value of δ is the critical value δ_c:

$$\delta_c=\alpha/e \qquad [16.6.27]$$

For values of δ less than δ_c there exist steady-state temperature distributions which satisfy Equation 16.6.26, but for values which exceed δ_c there are no such steady states and thermal explosion occurs.

At the other extreme, as α becomes very high Equation 16.6.24 reduces to

$$\ln\delta=\ln\frac{2D^2}{\cosh^2 D} \qquad [16.6.28]$$

Equation 16.6.28 also implies that δ passes through a maximum with D. This maximum occurs at

$$D=\coth D=1.2 \qquad [16.6.29]$$

which gives a value for δ_c of 0.88.

Values of δ_c, θ_o and θ_s for a slab over the whole range of α have been obtained by P.H. Thomas (1958) and are shown in Figure 16.38. The figure also gives the

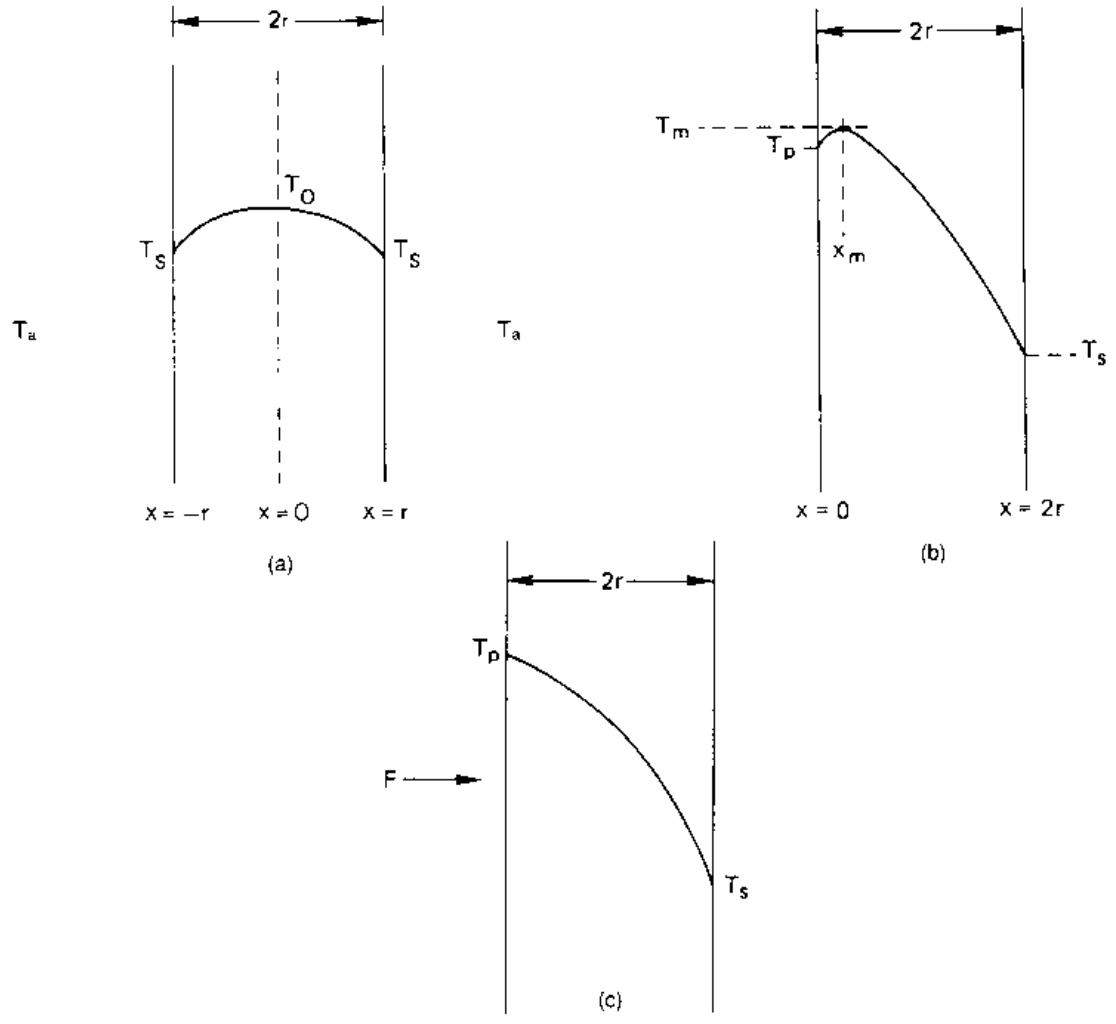


Figure 16.37 *Steady-state temperature profiles in a slab undergoing self-heating: (a) symmetrical slab; (b) asymmetrical slab with constant temperature at a hot face; and (c) asymmetrical slab with constant heat flux at hot face*

corresponding values for a cylinder and a sphere. The limiting values are:

	$\alpha \to 0$		$\alpha \to \infty$	
	δ_c	θ_o	δ_c	θ_o
Plane slab	α/e	1	0.88	1.19
Cylinder	$2(\alpha/e)$	1	2.00	1.39
Sphere	$3(\alpha/e)$	1	3.32	1.61

16.6.7 Model for a cylinder

Another principal configuration is the infinite cylinder. From Equation 16.6.17, setting $j = 1$

$$\frac{d^2\theta}{\delta z^2} + \frac{1}{z}\frac{d\theta}{dz} = -\delta \exp \theta \qquad [16.6.30]$$

Assuming a finite heat transfer coefficient, the boundary conditions are those given in Equation 16.6.19.

The general solution is

$$\theta = \ln\left[\frac{8B}{\delta(1 + Bz^2)^2}\right] \qquad [16.6.31]$$

where B is a constant of integration. Then from boundary condition 16.6.19b

$$\ln \delta = \ln\left[\frac{8B}{(B+1)^2}\right] - \frac{4B}{\alpha(B+1)} \qquad [16.6.32]$$

The maximum value of δ occurs at

$$\alpha = \frac{4B_c}{1 - B_c^2} \qquad [16.6.33]$$

where the subscript c denotes critical.

Then, utilizing this value of α, the parameters δ_c and θ_s may be obtained from Equations 16.6.31 and 16.6.32].

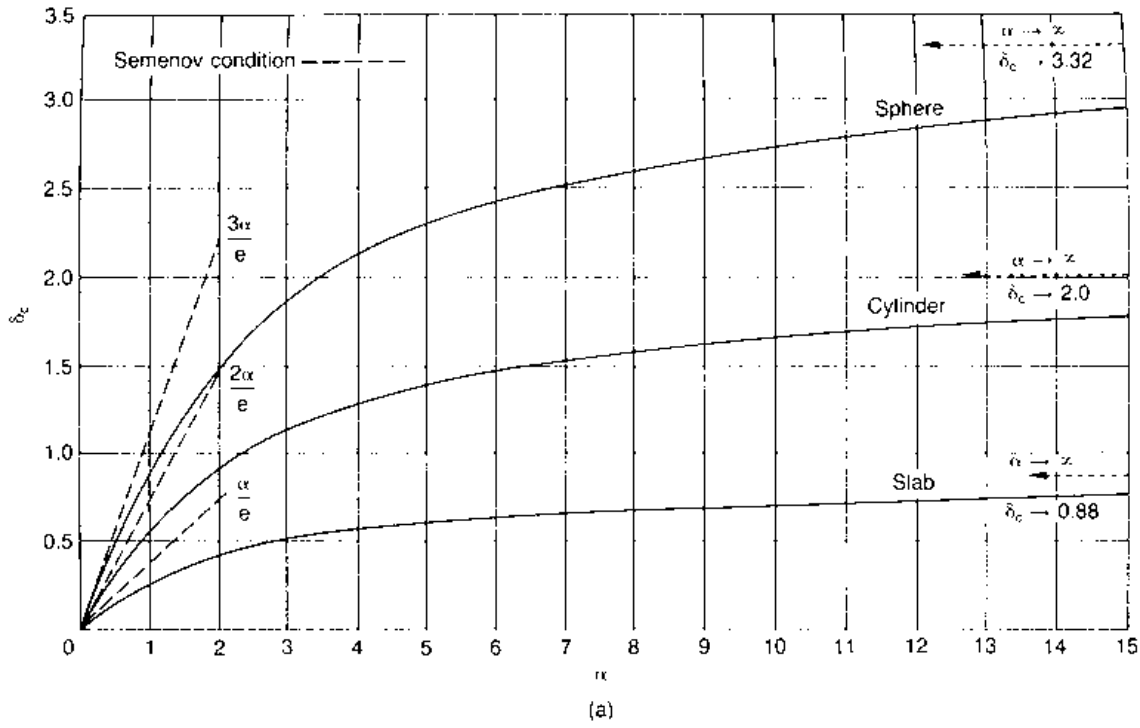


Figure 16.38 *Parameters governing self-heating without reactant consumption for three principal centrisymmetric shapes (P.H. Thomas, 1958): (a) critical values δ_c of the self-heating parameter.*

16.6.8 General model for slab, cylinder and sphere

A general steady-state model for the symmetrical slab, cylinder and sphere may be obtained from Equation 16.6.17.

The further approximation is introduced:

$$(j+1)\beta\theta \approx \delta \exp\theta \qquad [16.6.34]$$

where β is an effective heat transfer coefficient. There is no simple relation for β, but

$$\beta \approx \alpha \qquad \alpha \ll 1 \qquad [16.6.35]$$

Then, utilizing Equation 16.6.34 in Equation 16.6.17

$$\frac{d^2\theta}{\delta z^2} + \frac{j}{z}\frac{d\theta}{dz} = -(1+j)\beta\theta \qquad [16.6.36]$$

It can be shown that

$$\beta = c_1^2 \qquad \text{Plane slab} \qquad [16.6.37a]$$

$$= \frac{c_2^2}{2} \qquad \text{Cylinder} \qquad [16.6.37b]$$

$$= \frac{c_3^2}{3} \qquad \text{Sphere} \qquad [16.6.37c]$$

where c_1 is the first root of

$$c_n \tan c_n = \alpha \qquad [16.6.38a]$$

c_2 is the first root of

$$c_n J_1(c_n) = \alpha J_o(c_n) \qquad [16.6.38b]$$

and c_3 is a solution of

$$c_n \coth c_n + \alpha - 1 = 0 \qquad [16.6.38c]$$

where J_o and J_1 are Bessel functions of the first kind and of order zero and one, respectively.

The parameter δ has a maximum at $\theta = 1$ so that

$$\delta_c = \frac{(j+1)\beta}{e} \qquad [16.6.39]$$

16.6.9 Model for an asymmetrical slab

Returning to the slab, an alternative situation is one face against a hot body and one exposed to the atmosphere. For this case, in addition to the heat transfer at the surface exposed to the atmosphere, it is necessary to consider different conditions at the hot face. One assumption is that there is a constant temperature at the hot face, another is that there is a constant heat flux at the hot face. The steady state temperature profiles for these two cases are shown in Figures 16.37(b) and (c), respectively.

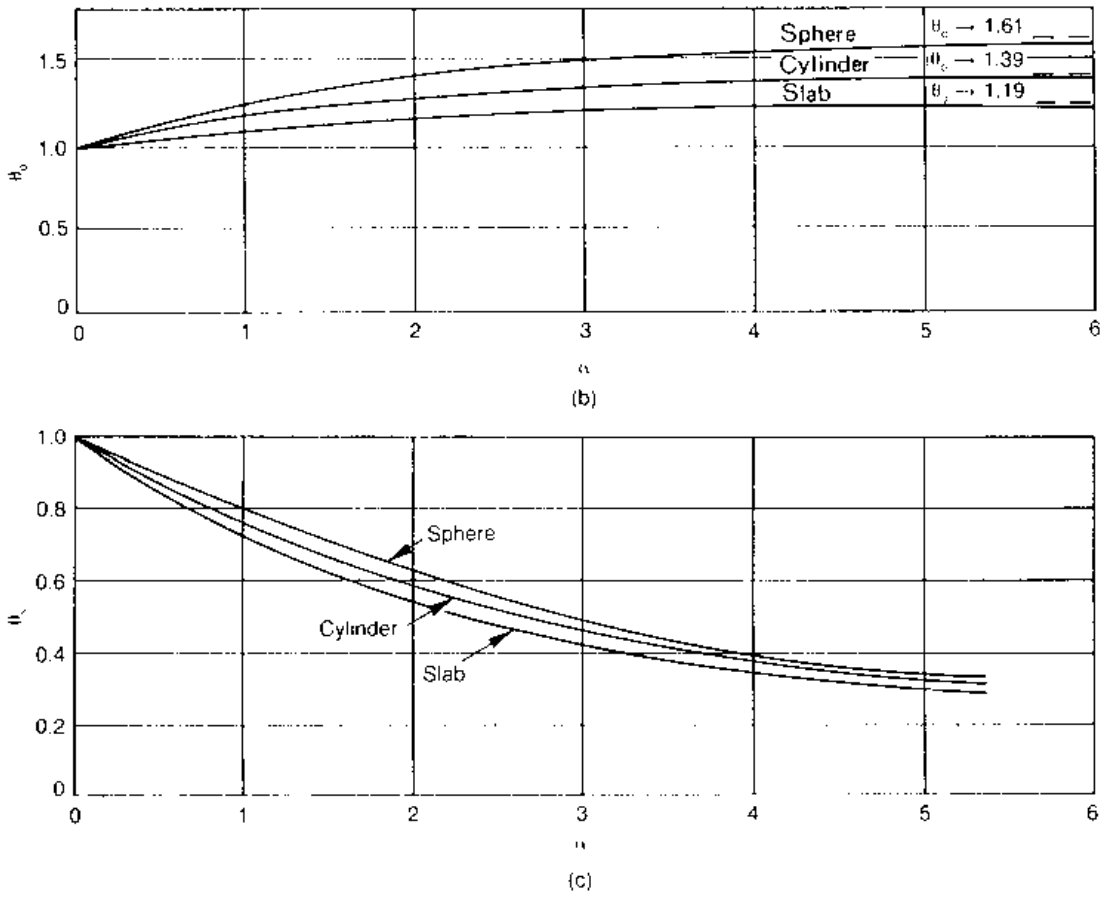


Figure 16.38 *(b) critical values of the dimensionless temperature θ_o at the centre; and (c) critical values of the dimensionless surface temperature θ_s (Courtesy of The Faraday Society)*

For the asymmetrical slab the dimensionless ignition parameter is defined as

$$\delta = \frac{E}{RT_p^2}\frac{r^2}{k}Q'\rho A \exp(-E/RT_p) \qquad [16.6.40]$$

and the dimensionless temperature difference as

$$\theta = \frac{E}{RT_p^2}(T - T_p) \qquad [16.6.41]$$

The relevant equation is Equation 16.6.18 and the general solution is Equation 16.6.20 and in addition

$$\frac{d\theta}{dz} = -(2\delta C_2)^{\frac{1}{2}} \tanh[z(\delta C_2/2)^{\frac{1}{2}} + C_1] \qquad [16.6.42]$$

The case considered here is that where the hot face is at a constant temperature and the surface of the other face is at a much lower temperature. For this case the boundary conditions are

$$z = 0;\ \theta = 0 \qquad [16.6.43a]$$

$$z = 2;\ \theta = \theta_s \qquad [16.6.43b]$$

Then from boundary condition 16.6.43a

$$C_1 = \pm\cosh^{-1}(C_2^{\frac{1}{2}}) \qquad [16.6.44a]$$

$$C_2 = \exp\theta_m \qquad [16.6.44b]$$

where subscript m denotes maximum.

From boundary condition 16.6.43b

$$(2\delta)^{\frac{1}{2}} = \frac{\cosh^{-1}[\exp(\theta_m/2) \pm \cosh^{-1}[\exp(\theta_m/2)\cdot\exp(-\theta_s/2)]}{\exp(\theta_m/2)} \qquad [16.6.45]$$

Given that the temperature of the surface is much less than that of the hot face, so that $\theta_s < 0$, it can be shown that $z_m \to 0$ and $\theta_m \to 0$, and that

$$(2\delta)^{\frac{1}{2}} = \cosh^{-1}[\exp(-\theta_s/2)] \qquad [16.6.46]$$

For large $|\theta_s|$ Equation 16.6.46 provides a good estimate of δ_c so that

$$\delta_c = \frac{(2\ln 2 - \theta_s)^2}{8} \quad [16.6.47a]$$

$$= \frac{(1.4 - \theta_s)^2}{8} \quad [16.6.47b]$$

Equation 16.6.47 is a good approximation for $|\theta_s|$ values as low as 8.

This argument suggests that for large $|\theta_s|$ it is permissible to adopt the approximation used by Zeldovitch and Semenov that the maximum temperature occurs at the hot face. Physically this means that the hot face is a perfect insulator instead of a perfect conductor of infinite thermal capacity.

The boundary conditions at the hot face then become

$$z = 0;\ \theta = 0 \quad [16.6.48a]$$

$$z = 0;\ \frac{d\theta}{dz} = 0 \quad [16.6.48b]$$

There is now only one steady-state temperature profile which is the critical one. With these boundary conditions

$$C_1 = 0 \quad [16.6.49a]$$

$$C_2 = 1 \quad [16.6.49b]$$

which gives Equation 16.6.47.

An alternative derivation in terms of the ambient temperature utilizes the boundary condition

$$z = 2;\ \frac{d\theta}{dz} = -\alpha(\theta_s - \theta_a) \quad [16.6.50]$$

with

$$\theta_a = \frac{E}{RT_p^2}(T_a - T_p) \quad [16.6.51]$$

and yields for $\theta_a < 0$ and large $|\theta_a|$

$$(2\delta_c)^{\frac{1}{2}} \tanh[(2\delta_c)^{\frac{1}{2}}] + 2\alpha \ln\{\cosh[(2\delta_c)^{\frac{1}{2}}]\} = -\alpha\theta_a \quad [16.6.52]$$

For $\delta_c > 5$, Equation 16.6.52 simplifies to

$$\delta_c \approx \frac{1}{2}\left(\frac{\alpha}{1+2\alpha}\right)^2 (1.4 - \theta_a)^2 \quad [16.6.53]$$

Equation 16.6.53 gives results of accuracy comparable to those of Equation 16.6.47 and simplifies to that equation as $\alpha \to \infty$.

For the assumption that the hot face is a perfect insulator, Equation 16.6.53 is valid for all values of α, but as an approximation to the more realistic case it fails at $\alpha = 0$.

16.6.10 Model for a hollow cylinder

Another important asymmetrical case is that of the hollow cylinder with the inner face at a constant hot temperature. For this case the dimensionless distances are defined as

$$z = r/r_1 \quad [16.6.54a]$$

$$z = r_1/r_1 = 1 \quad \text{Inner face} \quad [16.6.54b]$$

$$z = r_2/r_1 = z_s \quad \text{Outer face} \quad [16.6.54c]$$

The dimensionless temperature difference θ is defined by Equation 16.6.41 and the dimensionless ignition parameter as

$$\delta = \frac{E}{RT_p^2}\frac{r_i^2}{k} Q' \rho A \exp(-E/RT_p) \quad [16.6.55]$$

The relevant equation is Equation 16.6.30 and the general solution is

$$\theta = \ln\left[\frac{2F^2 G z^{F-2}}{\delta(1 + Gz^F)^2}\right] \quad [16.6.56]$$

where F and G are constants of integration.

The boundary conditions are

$$z = 1;\ \theta = 0 \quad [16.6.57a]$$

$$z = 1;\ \frac{d\theta}{dz} = 0 \quad [16.6.57b]$$

$$z = z_s;\ \theta = \theta_s \quad [16.6.57c]$$

From boundary condition 16.6.57b

$$F\frac{1-G}{1+G} = 2 \quad [16.6.58]$$

From Equations 16.6.56 and 16.6.58

$$\delta_c = \frac{8G}{(1-G)^2} \qquad 0 < G < 1 \quad [16.6.59]$$

From Equation 16.6.56 and boundary condition 16.6.57c

$$\theta_s = \ln\left[\frac{2F^2 G z_s^{F-2}}{\delta_c(1 + Gz_s^F)^2}\right] \quad [16.6.60]$$

For the critical ignition parameter δ_c^* expressed in terms of the half thickness of the cylinder wall is

$$\delta_c^* = \delta_c\left(\frac{z_s - 1}{z}\right)^2 \quad [16.6.61]$$

For a solid cylinder $F = 2$ and Equation 16.6.56 then reduces to Equation 16.6.31.

The model for the hollow cylinder may be applied to the problem of the self-heating of lagging on a pipe. The maximum, or critical, thickness of lagging to avoid self-heating may be calculated as follows. Calculate δ from Equation 16.6.55, assume that this is the critical value of δ ($\delta = \delta_c$), calculate G and then F from Equations 16.6.59 and 16.6.58. Then assume a normalized outer radius z_s and calculate θ_s from Equation 16.6.60. If θ_s differs from that specified, assume a fresh value of z_s and recalculate.

Some illustrative calculations have been made by Gugan (1974a) and are summarized in Table 16.29. The results show that if the pipe temperature is increased, the thickness of lagging needs to be decreased in order to avoid self-heating. Thus the relation between pipe temperature and lagging thickness is the reverse of that required for heat insulation.

16.6.11 Critical parameters

The parameter δ is given by Equation 16.6.10 which may be written as

$$\delta = \frac{E}{RT_a^2}\frac{r^2}{k} Q(T_a) \quad [16.6.62]$$

Table 16.29 *Illustrative calculation of the critical thickness of lagging to avoid self-heating (after Gugan, 1974a) (Courtesy of the Institution of Chemical Engineers)*

Parameters assumed	
$Q' = 2000\,\text{cal/g}$	$r_i = 5.08\,\text{cm}$
$\rho = 0.03\,\text{g/cm}^3$	$E = 6000\,\text{cal/mol}$
$A = 0.04\ \text{s}^{-1}$	$R = 1.987\,\text{cal/mol K}$
$k = 10^{-4}\,\text{cal/cm s°C}$	
$T_s \not> 313\,\text{K}$	
$T_p = 473\,\text{K}$ Case 1	
$573\,\text{K}$ Case 2	
Calculation results	
Case 1:	
$\delta_c = 14.1$	
$G = 0.479$	
$F = 5.68$	
$\theta_s = -2.21$	$T_s = 309\,\text{K}$
$z_s = 1.75$	$r_s = 8.6\,\text{cm}$
Case 2:	
$\delta_c = 29.3$	
$G = 0.596$	
$F = 7.91$	
$\theta_s = -2.48$	$T_s = 304\,\text{K}$
$z_s = 1.55$	$r_s = 7.8\,\text{cm}$

For a slab, Equation 16.6.62 may be rewritten utilizing Equation 16.6.14 and

$$\frac{V}{S} = r \qquad [16.6.63]$$

as

$$\delta = \frac{E}{RT_a^2}\,\frac{\alpha}{h}\,\frac{V}{S}\,Q(T_a) \qquad [16.6.64]$$

Further, since

$$\theta_o = \frac{E}{RT_a^2}(T_o - T_a) \qquad [16.6.65]$$

$$\delta = \theta_o \frac{r}{k}\,\frac{V}{S}\,\frac{Q(T_a)}{(T_o - T_a)} \qquad [16.6.66]$$

or

$$\delta = \theta_o \frac{\alpha}{h}\,\frac{V}{S}\,\frac{Q(T_a)}{(T_o - T_a)} \qquad [16.6.67]$$

Equation 16.6.67 can be extended to the other geometries by the generalization

$$\delta = (j+1)\theta_o \frac{r}{k}\,\frac{V}{S}\,\frac{Q(T_a)}{(T_o - T_a)} \qquad [16.6.68]$$

since

$$\frac{V}{S} = \frac{r}{2} \qquad \text{Cylinder} \qquad [16.6.69a]$$

$$\frac{V}{S} = \frac{r}{3} \qquad \text{Sphere} \qquad [16.6.69b]$$

or generally for the three principal symmetrical shapes

$$\frac{Sr}{V} = 1 + j \qquad [16.6.70]$$

These equations show that for these geometries the value of δ is a function of the surface/volume ratio *S/V*.

The relation between δ_c and *S/V* is illustrated in the table given in Section 16.6.6. As $\alpha \to 0$, δ_c is exactly proportional to *S/V*; whilst as $\alpha \to \infty$, δ_c lies within 10% of *S/V*.

There are a number of methods available for the estimation of the critical parameters δ_c and θ_o. One approximate analytical method has been developed by Boddington, Gray and Harvey (1971b). This method is based on the application of Equation 16.6.17 to any centrisymmetric convex body. The parameters are expressed in terms of an average radius R_o and of the shape factor j and procedures are given for determining these. At criticality, the following relations hold:

$$\delta_c(r) = \delta_c(R_o)\frac{r^2}{R_o^2} \qquad [16.6.71]$$

$$\theta_o = 2\ln[(j+7)/4] \qquad [16.6.72]$$

with

$$\delta_c(R_o) = 3F(j) \qquad [16.6.73]$$

$$F(j) = \frac{2j+6}{j+7} \qquad [16.6.74]$$

For the three principal symmetrical shapes the shape parameter has its usual values (0, 1 or 2) and

$$\frac{r^2}{R_o^2} = \frac{j+1}{3} \qquad [16.6.75]$$

Another approximate analytical method has been given by Hardee, Lee and Donaldson (1972). Other methods include expansion about the maximum temperature and use of a step function. Numerical solutions have also been obtained. In particular, results for the principal geometries have been given by Enig and co-workers (Enig, 1956; Enig, Shanks and Southworth, 1956). Results for some of the principal cases are summarized in Table 16.30.

The self-heating parameter δ is a function of the parameters of the reaction and solid mass and of the ambient temperature. There exists, therefore, a critical value of the ambient temperature which gives a critical value δ_c for the self-heating parameter. As the parameter $\alpha \to \infty$, there is a corresponding critical value of the surface temperature.

16.6.12 Oxidative self-heating

The self-heating reaction is usually, though not invariably, an oxidative one. Then the reaction will typically be governed by the reaction kinetics relation and by the diffusion of oxygen from the atmosphere.

There is relatively little information on the oxidation reactions which occur in self-heating. Models of the reaction frequently assume that it is first order with respect to oxygen concentration with a reaction index $n = 1$. For a number of reactions studied the value of the index n is about 0.7. Others are zero order over a wide range of oxygen concentrations. It is usual to assume

Table 16.30 *Selected critical values of the ignition parameter δ_c and the centre temperature θ_o without reactant consumption for centrisymmetric shapes*

Shape	*Dimension*	ϵ	α	δ_c	θ_o	*Method*[a]	*Reference*
Plane slab, infinite	Thickness $2r$	0	0	α/e	1	FK	P.H. Thomas (1958)
		0	∞	0.88	1.19	FK	P.H. Thomas (1958)
		0	∞	0.86	1.119	BGH[a]	Boddington, Gray and Harvey (1971b)
		0.02	∞	0.90	1.24	Numerical	Enig, Shanks and Southworth (1956)
		0.06	∞	0.94	1.37	Numerical	Enig, Shanks and Southworth (1956)
Cylinder, infinite	Radius r	0	0	$2\alpha/e$	1	FK	P.H. Thomas (1958)
		0	∞	2.00	1.39	FK	P.H. Thomas (1958)
		0	∞	2.00	1.39	BGH	Boddington, Gray and Harvey (1971b)
		0.02	∞	2.04	1.45	Numerical	Enig, Shanks and Southworth (1956)
		0.06	∞	2.15	1.61	Numerical	Enig, Shanks and Southworth (1956)
Sphere	Radius r	0	0	$3\alpha/e$	1	FK	P.H. Thomas (1958)
		0	∞	3.32	1.61	FK	P.H. Thomas (1958)
		0	∞	3.33	1.62	BGH	Boddington, Gray and Harvey (1971b)
		0.02	∞	3.40	1.68	Numerical	Enig, Shanks and Southworth (1956)
		0.06	∞	3.57	1.87	Numerical	Enig, Shanks and Southworth (1956)
Cube	Side $2r$	0	-[b]	2.52	1.89	Numerical	Parks (1961)[c]
		0.02	-	2.58		Numerical	Parks (1961)
		0.06	-	2.68		Numerical	Parks (1961)
Right cylinder	Radius r, height $2d$ $p = r/d$	0	∞	See formula in footnote[d]			
Cuboid[e]	Sides $2a$, $2b$, $2c$ $p = b/a$; $q = c/a$	0	∞	See formula in footnote[f]			

[a] BGH, Boddington, Gray and Harvey method; FK, Frank-Kamenetsky formulation.
[b] Values of δ_c quoted are those given by Bowes (1984). The corresponding values of α are not given, but Parks gives results for the range $\alpha = 20 - 100$.
[c] Corrected by Boddington, Gray and Harvey (1971b) and quoted by Bowes (1984).
[d] Bowes gives the relation: $\delta_c \approx 2.0 + 0.84p^2$.
[e] Also referred to as a rectangular brick.
[f] Bowes gives the relation: $\delta_c \approx 2.0 + 0.84(1 + 1/p^2 + 1/q^2)$.

that the Arrhenius equation applies, but Bowes warns that it is not always appropriate.

For oxidative self-heating it can be shown by a steady-state analysis that at critical conditions the value of the dimensionless temperature difference θ_o is given by

$$(1 + \epsilon\theta_o)^2\left[1 + (n-1)\frac{\theta_o}{\xi}\right] = \theta_o\left(1 - \frac{\theta_o}{\xi}\right) \qquad [16.6.76]$$

with

$$\theta_o = \frac{E}{RT_a}(T_o - T_a) \qquad [16.6.77]$$

$$\xi = \frac{E}{RT_a}\frac{Q^* D_p C_o}{k} \qquad [16.6.78]$$

where C_o is the concentration of oxygen in the atmosphere, D_p is the diffusion coefficient of oxygen in the pores, n is the index of the concentration term, Q^* is a modified heat release per unit mass, T_o is the temperature at the centre, θ_o is the dimensionless temperature difference at the centre and ξ is a parameter.

16.6.13 Effect of water

Organic materials tend to be hygroscopic and commonly contain some 10–20% water as a condensed phase. Water can have a strong effect on self-heating but its effect is somewhat complex. Reviews have been given by Walker (1967) and Bowes (1984).

Some of the effects are chemical. Water increases the rate of oxidation of many materials. In some cases, however, there can be an inhibiting effect.

Other effects are physical. Water has a high latent heat of vaporization and a correspondingly high heat of adsorption. During self-heating it vaporizes in the hotter regions and condenses again in the cooler regions. The net effect is an appreciable increase in the rate of heat transfer. The presence of water thus increases the effective thermal conductivity of the material. The increase may be by an order of magnitude.

The increase in temperature in the hotter region is retarded by the presence of water as vaporization takes place. The effect usually occurs at temperatures in the range 60–90°C, which is generally well below the temperature at which thermal ignition occurs. Thus this effect tends to manifest itself as an increase in the induction time.

If the vaporization of water occurs fairly uniformly over the temperature range as the material undergoes self-heating, the effect is to reduce the effective heat of reaction. In some cases this may result in the suppression of thermal ignition. This effect is seen in the case of 'overdried' materials. If a material is dried down to a very low water content, the reduction in the effective heat of reaction just described is no longer operative, and the material becomes more prone to thermal ignition.

There is also another effect of water on overdried material. When the material is first exposed to the atmosphere, water is adsorbed and heat is released. This may cause a temperature rise in cool material or may delay a temperature fall in hot material. In either case the base temperature from which any self-heating process starts is increased.

16.6.14 Unsteady-state model

The treatment of self-heating given so far has been based on the assumption of steady state. There are a number of situations in which this assumption breaks down and for which it is necessary to adopt a unsteady-state approach. These include:

(1) reactant consumption;
(2) induction period;
(3) autocatalytic reactions;
(4) hot spots and hot materials;
(5) high ambient temperature;
(6) varying ambient temperature.

The basic equation for self-heating is the unsteady-state Equation 16.6.1 with Equation 16.6.2. This latter equation may be modified to make explicit the dependence on reactant consumption, and then takes the form of Equation 16.6.81.

Consideration is now given to some of the principal aspects of the unsteady state, namely reactant consumption, induction period, autocatalytic reactions, and hot spots and hot materials.

16.6.15 Reactant consumption

In general the reaction equation will be of the form

$$\frac{dC}{dt} = -C^n A \exp(-E/RT) \qquad [16.6.79a]$$

$$\frac{dC}{dt} = -\psi(C) A \exp(-E/RT) \qquad [16.6.79b]$$

with

$$\psi(C) = C^n \qquad [16.6.80]$$

Then Equation 16.6.2 becomes

$$Q = C^n Q'' A \exp(-E/RT) \qquad [16.6.81a]$$

$$= \psi(C) Q'' A \exp(-E/RT) \qquad [16.6.81b]$$

where C is the concentration of oxygen, Q'' is the modified heat released per unit volume, ψ is a concentration function and n is an index.

Then Equation 16.6.3 becomes

$$\rho c \frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{j}{x}\frac{\partial T}{\partial x}\right) + C^n Q'' A \exp(-E/RT) \qquad [16.6.82]$$

Introducing the dimensionless concentration

$$\omega = C/C_o \qquad [16.6.83]$$

where C_o is the concentration of oxygen in the ambient air and ω is the dimensionless concentration, and an alternative form of the dimensionless ignition parameter

$$\delta = \frac{E}{RT_a}\frac{r^2}{k} C_o^n Q'' A \exp(-E/RT_a) \qquad [16.6.84]$$

Equation 16.6.82 becomes

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial z^2} + \frac{j}{z}\frac{\partial \theta}{\partial z} + \delta \omega^n \exp[\theta/(1+\epsilon\theta)] \qquad [16.6.85]$$

and Equation 16.6.79 becomes

$$\frac{d\omega}{d\tau} = -\frac{\delta}{B}\omega^n \exp[\theta/(1+\epsilon\theta)] \qquad [16.6.86]$$

with

$$B = \frac{E}{RT_a^2}\frac{C_o Q''}{\rho c} \qquad [16.6.87]$$

where B is a dimensionless parameter. The parameter B may be interpreted as a dimensionless adiabatic temperature rise.

For the three principal symmetrical shapes and for general case of finite α the usual boundary conditions for Equation 16.6.85 are

$$z = 0;\ \frac{d\theta}{dz} = 0 \qquad [16.6.88a]$$

$$z = 1;\ \frac{d\theta}{dz} = -\alpha\theta_s \qquad [16.6.88b]$$

and the initial conditions are

$$\tau = 0;\ \theta = 0;\ \omega = 1 \qquad [16.6.89]$$

The behaviour of a self-heating mass may be characterized in terms of the parameters B and δ as shown in Figure 16.39. For large values of B, shown in Figure 16.39(a), the profiles of θ are sensitive to δ and there is a value of δ at which there is a relatively sharp transition to thermal explosion. For small values of B, shown in Figure 16.39(b), the profiles of θ are less sensitive, thermal explosion is less well defined and may not occur at all.

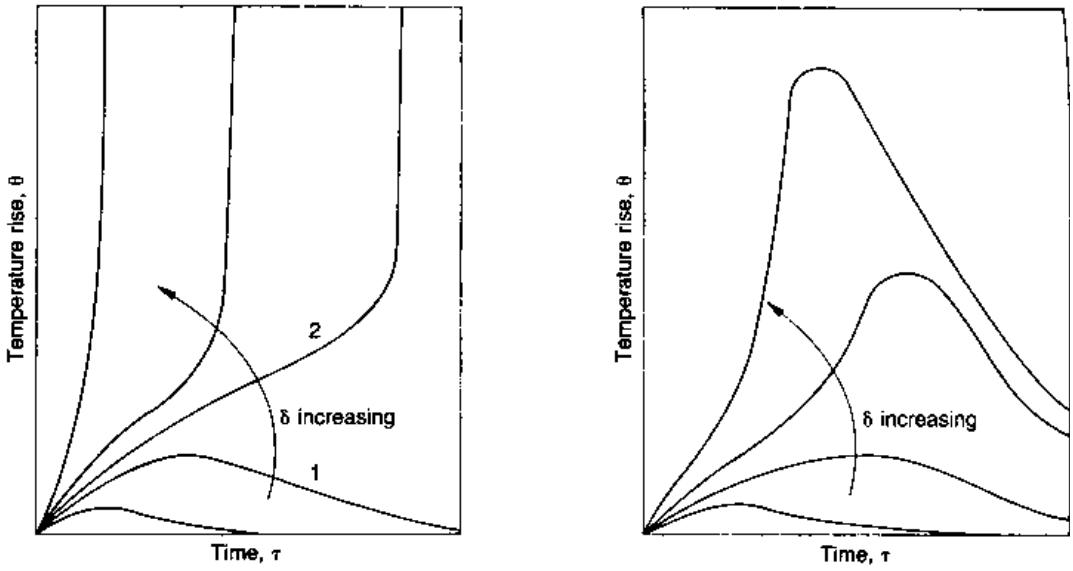


Figure 16.39 *Effect of parameters governing self-heating with reactant consumption (Bowes, 1984). (a) Large B; differences between curves 1 and 2 can result from small changes in δ. (b) Small B; differences between curves can result from large changes in δ (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

Table 16.31 *Selected critical values of the ignition parameter δ_c with reactant consumption for centrisymmetric shapes (after Tyler and Wesley, 1967) (Courtesy of the Combustion Institute)*

		Cylinder			*Sphere*		
n	B	$\epsilon = 0$	*0.025*	*0.05*	$\epsilon = 0$	*0.025*	*0.05*
0	-	2.000	2.057	2.119	3.322	3.420	3.527
1	1000	2.052	2.113	2.180	3.405	3.510	3.626
1	100	2.248	2.328	2.417	3.722	3.859	4.013
1	25	2.729	2.860	3.010	4.491	4.713	4.965
2	1000	2.082	2.145	2.215	3.453	3.563	3.684
2	100	2.403	2.498	2.606	3.971	4.134	4.321
2	25	3.255	3.443	3.651	5.309	5.610	5.937

It is possible to derive a relation for the critical value δ_c as a function of B and n. Let $\delta(B)$ be the initial value δ and $\delta_c(\infty)$ be the critical value of δ at the end of the induction period for $B = \infty$. Then it can be shown that

$$\delta_c(B,n) = \frac{\delta_c(\infty)}{1 - 2.7(n/B)^{2/3}} \qquad [16.6.90a]$$

$$\delta_c(B,n) = \delta_c(\infty)(1 + 2.7(n/B)^{2/3}) \qquad B \to \infty \qquad [16.6.90b]$$

The effect of reactant consumption has been studied, particularly for the three principal symmetrical shapes. Results for the centri-symmetric shapes obtained by Tyler and Wesley (1967) using numerical integration are shown in Table 16.31.

16.6.16 Induction period

It is possible to define a number of induction periods. One period of particular interest is the total time from the initiation of a situation leading to thermal explosion to the explosion itself. It is this induction period which is considered here.

A treatment of the induction period, assuming no reactant consumption, has been given by Zinn and Mader (1960), who performed numerical integration of Equation 16.6.12 for the following case. A body at initial temperature T_i has its surface suddenly raised to a temperature T_s which exceeds the critical value T_c for thermal explosion. They defined a dimensionless induction period τ_i such that

$$\tau_i = \frac{kt_i}{\rho c r^2} \qquad [16.6.91]$$

where t_i is the induction period and τ_i is the dimensionless induction period. They obtained for the three principal symmetrical shapes the results shown in Figure 16.40. The induction period decreases as the surface temperature increases.

If the surface temperature is raised to one greatly in excess of the critical value, the temperature rise in the solid occurs near the surface rather than at the centre. Zinn and Mader examined this situation also and obtained for the case of a 1 in. sphere of cyclotrimethylene trinitramine, or RDX explosive the results shown in Figure 16.41.

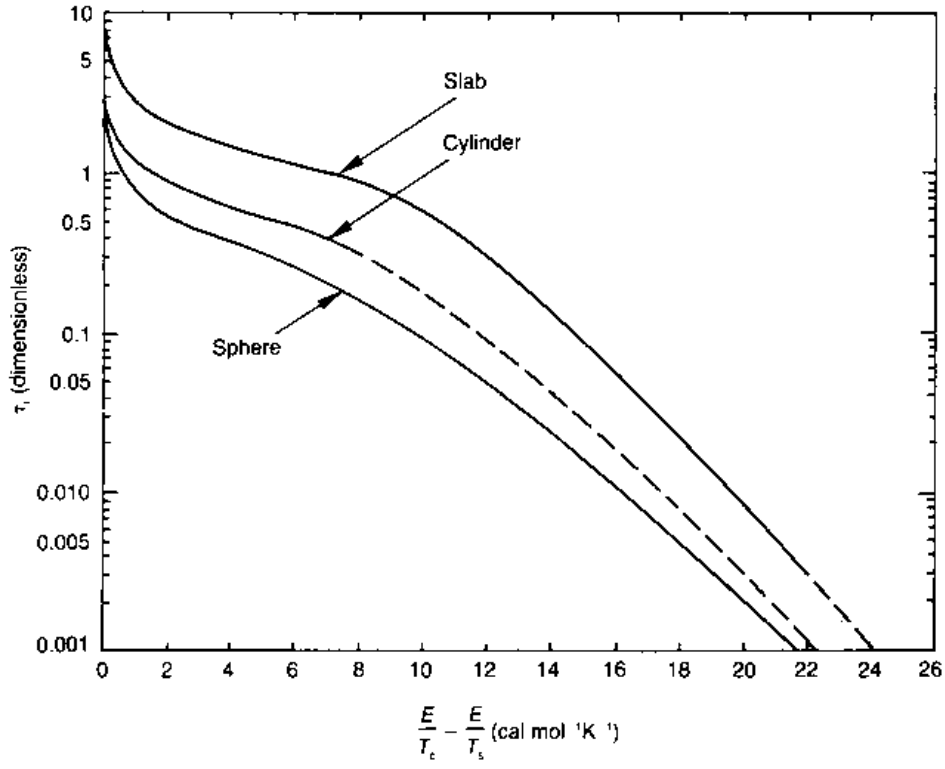


Figure 16.40 *Induction period for self-heating without reactant consumption for three principal centrisymmetric shapes (Zinn and Mader, 1960). Initial temperature $T_o = 298\,K$ ($< T_c$) (Courtesy of the Journal of Applied Physics)*

It has been shown that the values of δ for the transition from a central to an annular explosion are approximately as follows:

	δ
Plane slab	9.25
Cylinder	12.25
Sphere	14.25

16.6.17 Autocatalytic reactions

In some cases the self-heating reaction is an autocatalytic one. For this case the reaction may be expressed as

$$\frac{d\phi}{dt} = k(\phi^* + \phi)(1 - \phi) \qquad [16.6.92]$$

where ϕ is the fractional conversion and ϕ^* is the small fractional conversion necessary to initiate the reaction.

A quantity χ may be defined as

$$\chi = \frac{\delta}{(1+j)\alpha} \qquad [16.6.93]$$

where χ may be interpreted broadly as the ratio of the rate of heat generation to the rate of heat loss.

The critical condition for thermal ignition is

$$\chi = \frac{4}{(1+\phi^*)^2 e} \qquad [16.6.94a]$$

$$\approx \frac{4}{e} \qquad [16.6.94b]$$

and the value of the critical ignition parameter δ_c is

$$\delta_c = \frac{4}{(1+\phi^*)^2} \frac{(1+j)\alpha}{e} \qquad [16.6.95]$$

16.6.18 Thermal explosions of the second kind

As already described, there exist both stable and unstable steady states. A thermal explosion of the second kind involves passage through an unstable steady state. This situation can occur where there is an additional heat source or where there are certain initial conditions. A typical additional heat source might be a wander lamp left lying in a pile of material in a silo. Another form of additional heat source is a parallel reaction. The situation involving initial conditions of particular interest are those relating to hot spots, which are now considered.

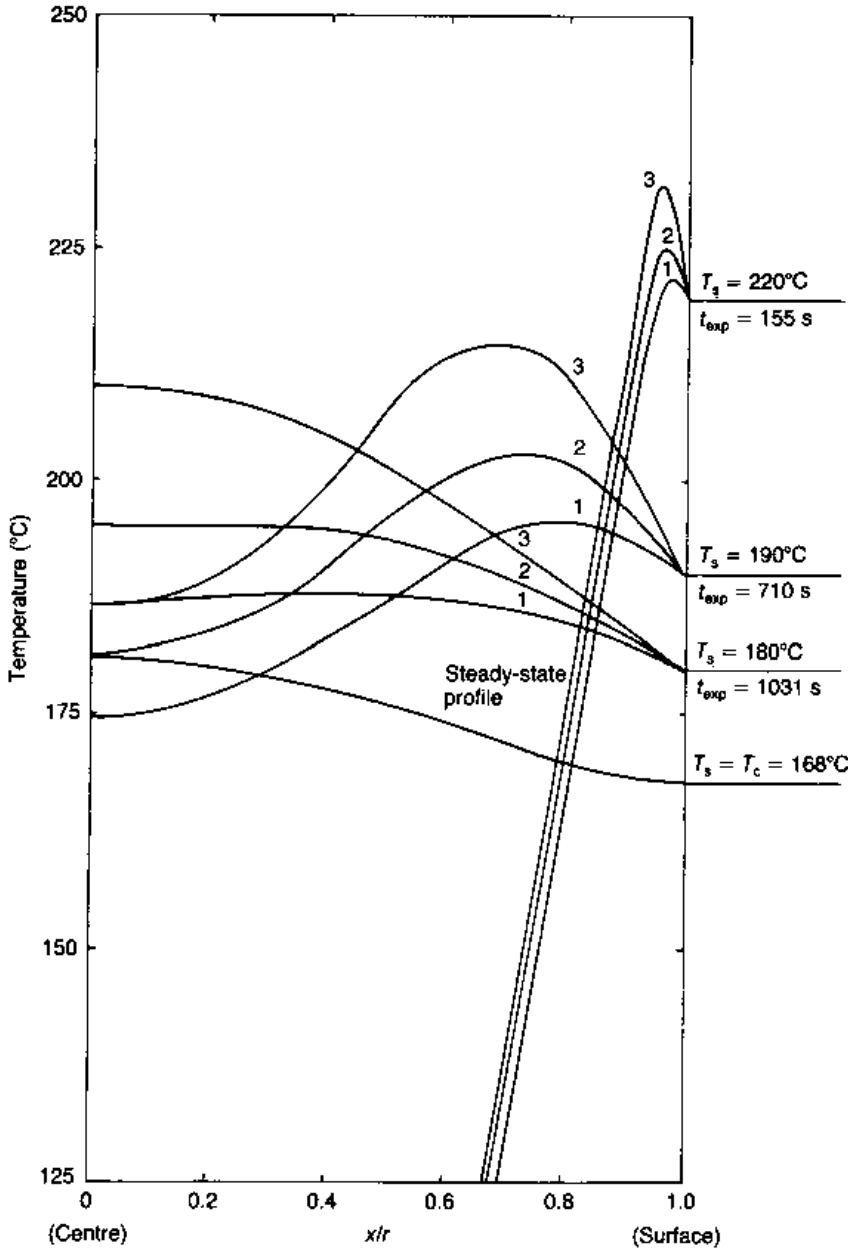


Figure 16.41 *Temperature profiles for a 1 in. sphere of RDX at times close to the end of the induction period (Zinn and Mader, 1960): (1) fraction of time to explosion 0.9; (2) fraction of time to explosion 0.95; (3) fraction of time to explosion 0.98. Initial temperature 25°C. The steady-state temperature profile at the critical temperature T_c is also shown (Courtesy of the Journal of Applied Physics)*

16.6.19 Hot spots and hot materials

The topic of hot spots includes the following cases: (1) reactive hot spots, (2) inert hot spots and (3) hot materials.

A hot spot is a limited volume in a mass of reactive material which is at a temperature above that of the material. The hot spot may be reactive or inert. A hot material in this context is one in which the whole mass of the material is above ambient temperature. It may be regarded as a form of reactive hot spot in which the hot region extends to the whole mass.

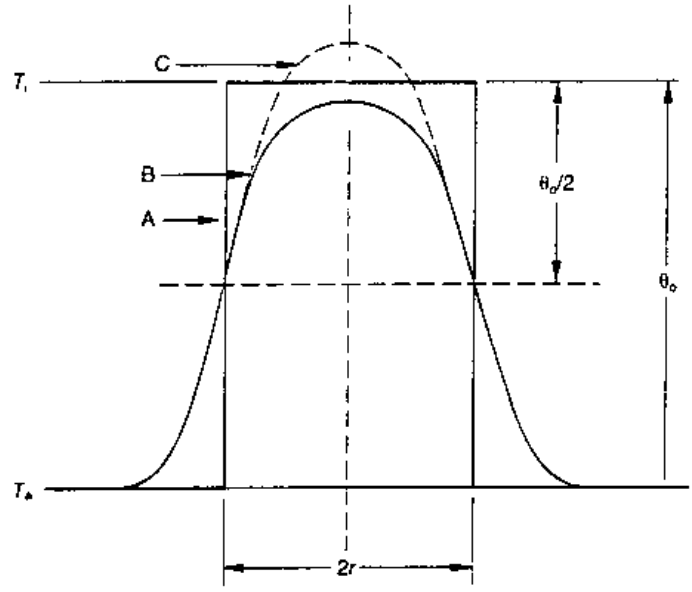


Figure 16.42 *Temperature profiles for a hot spot: A, initial temperature profile of hot spot, reactive or inert; B typical early temperature profile for inert hot spot; and C, typical early temperature profile for reactive hot spot*

The temperature profiles in a hot spot with a 'square' initial temperature distribution are shown in Figure 16.42. The initial temperature profile is given by outline A. An inert hot spot will lose heat to the surrounding medium and the temperature distribution in the early period may then be expected to take a form such as that shown in curve B. A reactive hot spot, however, will generate some heat and, assuming this is appreciable, its temperature distribution in the early period may be expected to take a form such as that shown by curve C.

For a reactive hot spot it has been shown by P.H. Thomas (1973a) that

$$\delta_c \approx \theta_o \psi'(\tau) \qquad [16.6.96]$$

with

$$\tau = 1/\delta_c \qquad [16.6.97]$$

where the parameters are defined in terms of the initial temperature T_i of the hot spot so that

$$\delta_c = \frac{E}{RT_i^2}\frac{r^2}{k}Q'\rho A \exp(-E/RT_i) \qquad [16.6.98]$$

$$\theta_i = \frac{E}{RT_i^2}(T_i - T_{im}) \qquad [16.6.99]$$

$$\psi = \frac{T_i - T}{T_i - T_{im}} \qquad [16.6.100]$$

$$\psi' = \frac{d\psi}{d\tau} \qquad [16.6.101]$$

where T_i is the initial temperature of the hot spot, T_{im} is the initial temperature of the medium, θ_i is the initial value of θ in the hot spot and τ is the dimensionless time.

Of particular interest is the solution of Equations 16.6.96–16.6.101 for hot material, where in effect the hot spot extends through the whole mass. In applying these equations use is made of the fact that in the early stages of cooling of an inert hot spot the temperature profiles all tend to intersect at a temperature $\theta_o/2$ as shown in Figure 16.42. Then the value of θ_o used in the treatments for hot materials is one-half of the value of θ_i as given by Equation 16.6.99.

Then for the case where $\alpha \to \infty$, P.H. Thomas (1972) has shown that

$$\psi'(\tau) \approx \frac{\exp(-1/4\tau)}{2\pi^{\frac{1}{2}}\tau^{\frac{3}{2}}} \qquad \text{Plane slab} \qquad [16.6.102]$$

$$\psi'(\tau) \approx \frac{\exp(-1/4\tau)}{4\pi^{\frac{1}{2}}\tau^{\frac{5}{2}}} \qquad \text{Sphere} \qquad [16.6.103]$$

$$\psi'(\tau) \approx \frac{3\exp(-1/4\tau)}{2\pi^{\frac{1}{2}}\tau^{\frac{3}{2}}}[\mathrm{erf}(1/2\tau^{\frac{1}{2}})]^2 \qquad \text{Cube} \qquad [16.6.104]$$

For this case the value of δ_c is obtained from Equation 16.6.96 utilizing Equations 16.6.102–16.6.104.

At the other extreme, for $\alpha \to 0$ it can be shown that

$$\psi = 1 - \exp(-\alpha S r \tau / V) \qquad [16.6.105]$$

Then, differentiating Equation 16.6.105 and utilizing Equation 16.6.70 for the three principal symmetrical shapes it is readily shown that

$$\delta_c = \alpha(1+j)\theta_o \exp[-\alpha(1+j)/\delta_c] \qquad [16.6.106a]$$

$$\delta_c \approx \alpha(1+j)\theta_o \qquad \theta_o \gg 1;\ \delta_c \gg 1 \qquad [16.6.106b]$$

Treatments for the inert hot spot tend to be more complex.

16.6.20 Determination of model parameters

The self-heating properties of a porous solid may be characterized in terms of (1) the minimum ignition temperature, (2) the critical characteristic length, (3) the surface heat transfer coefficient and (4) the induction period.

The minimum ignition temperature may be obtained by exposing a body of the material in a defined shape to a series of successively higher temperatures using calorimetric methods and determining the temperature which is just high enough for ignition to occur.

For the critical characteristic length use is made of Equation 16.6.10 with the ignition parameter taken as the critical value δ_c and rearranged to give

$$\ln\left(\frac{\delta_c T_a^2}{r^2}\right) = M - \frac{P}{T_a} \qquad [16.6.107]$$

with

$$M = \ln(Q'\rho AE/Rk) \qquad [16.6.108]$$

$$P = E/R \qquad [16.6.109]$$

where R is the universal gas constant, T_a is the absolute temperature of the air and M and P are parameters.

Then if experiments are conducted with a range of slabs of different sizes and different surface temperatures, pairs of values of r and T_a are obtained. A plot of $\ln(\delta_c T_a^2/r^2)$ vs $1/T_a$ then gives the values of M and P.

Such experiments are in fact usually done using cubes rather than slabs. For a cube, δ_c is 2.6 so that the relation between the critical characteristic length for a cube r_{cb} and for a slab r_{sb} is

$$r_{sb} = r_{cb}(0.88/2.6)^{\frac{1}{2}} \qquad [16.6.110]$$

The commonly used test for the determination of the self-heating parameters M and P is to heat up a cube of the material in an oven under standard conditions and to measure the temperatures in the cube.

For the surface heat transfer coefficient, and hence the Biot number, use is made of Equation 16.6.5. The heat transfer coefficient for convection depends on the shape of the body and on whether the convection is natural or forced. For the case of natural convection and for a small sphere

$$\mathrm{Nu} \approx 2.0 + 0.6\ \mathrm{Pr}^{0.33}\ \mathrm{Gr}^{0.25} \qquad [16.6.111a]$$

For air, for which $\mathrm{Pr} \approx 0.7$, Equation 16.6.111a can be approximated by

$$\mathrm{Nu} \approx 2.0 + 0.6(\mathrm{Pr}\ \mathrm{Gr})^{0.25} \qquad [16.6.111b]$$

$$= 2.0 + 0.6\ \mathrm{Ra}^{0.25} \qquad [16.6.111c]$$

with

$$\mathrm{Nu} = \frac{dh_c}{k_f} \qquad [16.6.112]$$

$$\mathrm{Pr} = \frac{\nu}{\alpha_f} \qquad [16.6.113]$$

$$\mathrm{Gr} = \frac{gad^3\Delta T}{\nu^2} \qquad [16.6.114]$$

$$\mathrm{Ra} = \frac{g}{\nu\alpha_f} d^3 \frac{\Delta T}{T} \qquad [16.6.115]$$

$$a = 1/T \qquad [16.6.116]$$

where a is the volume coefficient of expansion, d is the diameter of the sphere, k_f is the thermal conductivity of the fluid, ΔT is the difference between the surface temperature and the ambient temperature $(T_s - T_a)$, α_f is the thermal diffusivity of the fluid and ν is the kinematic viscosity of the fluid. Gr, Nu, Pr and Ra are the Grashof, Nusselt, Prandtl and Rayleigh numbers, respectively.

Then from Equations 16.6.111c, 16.6.112 and 16.6.115

$$h_c = \frac{k_f}{d}(2.0 + 0.6\ \mathrm{Ra}^{0.25}) \qquad [16.6.117]$$

The first term in the brackets in Equation 16.6.117 represents film conduction and the second term represents convection.

The heat transferred by radiation q is

$$q = \frac{\epsilon_1\epsilon_2}{\epsilon_1 + \epsilon_2 - \epsilon_1\epsilon_2}\sigma(T_s^4 - T_a^4) \qquad [16.6.118]$$

where ϵ_1 is the emissivity of the surface and ϵ_2 is that of the surroundings.

Differentiating Equation 16.6.118 with respect to T_a, and linearizing

$$\frac{dq}{dT_a} = 4\frac{\epsilon_1\epsilon_2}{\epsilon_1 + \epsilon_2 - \epsilon_1\epsilon_2}\sigma T_a^3 \qquad [16.6.119a]$$

$$= h_r \qquad [16.6.119b]$$

As an approximation, the values of ϵ_1 and ϵ_2 in Equation 16.6.119a may be taken as unity.

Bowes gives the following values for a sphere:

r (mm)	$0.6\ \mathrm{Ra}^{0.25}$	h_c (W/m^2 K)	h_r (W/m^2 K)	α	δ_c
1.6	0.87	39	47	2.7	1.80
25.4	8.2	7.1	21	14.1	2.90
279	54	3.2	12.6	88	3.24

In Equation 16.6.117 for the convection heat transfer coefficient the dominant term is the film term at the smaller diameters and the convection term at the larger diameters.

The induction period may be determined by experiment. The results of a number of experiments follow the relation

$$t_i \propto r^2 \qquad [16.6.120]$$

Alternatively, the induction period may be estimated from Figure 16.40.

A material liable to self-heating is often a powder and its self-heating properties therefore depend on the particle size distribution. Experimental determinations of self-heating parameters are valid only for similar material.

16.6.21 Precautions against self-heating

Prevention of self-heating depends on recognition of the hazard, design features, and good housekeeping and adherence to procedures.

If a material may be liable to self-heating, tests may be done to determine first whether this is the case, and, if so, the critical size. Bowes gives the following broad rules of thumb for liability to self-heating in terms of the critical dimension r_c:

$r_c \geq 40$ m Material not liable to self-heating

$r_c \leq 10$ m Material liable to self-heating

Materials leaving the process hot can be cooled before being sent to storage. Self-heating of materials in storage and transport can be prevented by using smaller containers and/or by remixing the material periodically. Where oxidative self-heating is involved, measures can be taken to reduce the oxygen content of the ambient gas. One approach is the use of atmosphere control and, in particular, of inerting. Another method is the use of an oxygen barrier such as plastic liners inside paper bags. Polyethylene has been successfully used to prevent self-heating. It is not, however, a totally effective oxygen barrier and may be of limited use for more reactive materials.

Factors which tend to increase safety include the presence of antioxidants and the limitation of the residence time. Conversely, the safety margin is reduced if there is a loss of antioxidants which are normally present or a rise in the residence time above the normal value.

Some materials, such as freshly made activated carbon, heat up appreciably during the first 24 hours after manufacture. The processes involved are probably sorption and oxidation of the most reactive sites. Such materials can be 'weathered' by allowing the material to stand for a period in separate, freshly filled bags.

Self-heating of lagging can be minimized by measures to prevent leaks and by use of suitable lagging thicknesses.

Special measures are required to deal with situations where there is a possibility of a leak such as the ethylene oxide leaks described in Section 16.6.2. Measures proposed following the investigation of these incidents include avoidance of dead leg pipework and other stagnant zones, reduction of the number of flanges and other possible leak points, measures to ensure leak-tight construction, use of non-absorbent lagging material if possible, inerting of regions at risk, provision of leak detection devices and regular testing for leak tightness and regular inspection for leaked materials. Large flanges may be installed without fire insulation but protected by sprinkler systems instead. The insulation used may be of the two-layer type with an inner material of close cell structure, such as cellular glass, and an outer layer of fire resistant material, with a vapour barrier between to prevent ingress of water and chlorides.

Good housekeeping can reduce self-heating caused by items such as waste rags or dust layers.

16.7 Static Electricity

Static electricity is an important source of ignition in process plants. There have been many apparently mysterious explosions the cause of which was eventually traced to static electricity. On the other hand there has been some tendency in investigations to attribute to static electricity ignitions for which no other cause could be found, even though the positive evidence for static was weak.

There is now much more information available both on the nature and on the prevention of static electricity. But despite this it remains a phenomenon which is often not well understood or appreciated. It is for this reason that a separate section is devoted here to static electricity rather than because it is a statistically dominant source of ignition.

Static electricity is a potential source of ignition wherever there is a flammable mixture of gas or of powder or dust. Accounts of static electricity are given in *Electrostatics in the Petroleum Industry* (Klinkenberg and van der Minne, 1958), *Handbuch der Raumexplosionen* (Freytag, 1965), *Handbook of Industrial Loss Prevention* (FMEC, 1967), *Electrostatic Hazards* (Haase, 1977), *Dust Explosions* (Cross and Farrer, 1982), *Electrostatics* (Cross, 1987), *Electrostatic Hazards and Powder Handling* (Glor, 1988) and *Understanding and Controlling Static Electricity* (Lüttgens and Glor, 1989) and by R.V. Wright (1964), J.C. Howard (1964), N. Gibson (1969), J.R. Hughes (1970), Napier (1971) and K.N. Palmer (1973a).

The relevant British Standard is BS 5958: 1991 *Code of Practice for Control of Undesirable Static Electricity* Part 1: 1991 *General Considerations* and Part 2: 1991 *Recommendations for Particular Industrial Situations*. In the USA, NFPA 77: 1988 *Static Electricity* applies.

Selected references on static electricity are given in Table 16.32.

16.7.1 Static electricity in industrial processes

The industrial situations in which undesired static charges are generated are largely those in which two surfaces move relative to each other, with initial contact followed by subsequent separation. When the surfaces are separated, one body tends to be left with a positive charge and the other with a negative charge. If the bodies are good conductors of electricity, the charge moves quite freely and both bodies are effectively restored to their original uncharged state through the last points of contact at separation. But if one or both of the bodies are poor conductors, the charge does not flow freely and both bodies retain charge after separation.

There are many industrial processes which involve surface contact, movement and separation of poorly conducting materials. These processes may be classified in terms of: the phases involved, e.g. gas–solid; the general type of system, e.g. dusts and powders; or the particular type of process or equipment, e.g. pneumatic conveying. Some systems in the process industries where static effects are important are listed, by the phases involved, in Table 16.33. The treatment given below is based on the general type of system. The hazard of static electricity occurs in the process industry in: fluid handling operations such as pipeline flow, settling of drops, agitation, filling of storage tanks, filling of tankers; powder and dust and powder handling operations such as grinding, sieving and pneumatic conveying; in sprays and mists such as in steam cleaning and steam leaks; moving equipment such as conveyor belts and bucket elevators; and the human body.

Table 16.32 *Selected references on static electricity*

Pauthenier and Moreau-Hanot (1932); Guest (1938 BM Bull. 638); Smythe (1939); Silsbee (1942); Klinkenberg and Mooy (1948); NFPA (1950); Cooper (1953a,b); P.H.S. Henry (1953, 1971b); Swann (1953); Bustin, Culbertson and Schleckser (1957); J.C. Howard (1958, 1959, 1964); Klinkenberg (1957, 1959, 1964b, 1967c, 1971); Klinkenberg and van der Minne (1958); McGuire (1958); Saletan (1959a,b); Trevana (1961); Anon. (1962a); Schön (1962a,b, 1965, 1967, 1968); Department of Labor (1963); L. Wright and Ginsburgh (1963, 1964); R.V.Wright (1964); Freytag (1965); Owens (1965); Durand (1966); Eichel (1967); Harper (1967a,b); Herzog (1967); Rees (1967); J.R. Hughes (1970); N. Gibson (1969, 1971, 1983, 1986a, 1990b); Hearfield (1970); Mahley (1971, 1972); Napier (1971); A.D. Moore (1973); K.N. Palmer (1973a); Strawson (1973); Napier and Rossell (1974); Anon. (1975 LPB 2, p. 1); Barreto (1975); Chubb, Pollard and Butterworth (1975); Horvath and Bertha (1975); Pesetsky and Fisher (1975); PITB (1975 Safety Training Guide 2); Rivera (1975); J.F. Wagner (1975); Bright (1977); Haase (1977); R. King and Magid (1979); Wada, Perlman and Kokado (1979); J.T. Leonard (1981); Cross and Farrer (1982); IBC (1982/29, 1983/43, 1991/80); Ramage, Swithendy and Ross (1982); Bustin and Dukek (1983); Anon. (1986j); Crowley (1986); Cross (1987); Pay (1987 LPB 78); Sproston (1987); Kalisvaart (1988 LPB 79); Lüttgens and Glor (1989); Hearn (1991); Britton (1992); Cartwright (1992); Dean *et al.* (1992); Pratt (1993, 1994 LPB 120)
BS 5958: 1991–

Prevention
NFPA (1950); Klinkenberg and van der Minne (1958); Shell Chemical Co. (1963); Aron (1964); Beach (1964–); Valko and Tesoro (1964); FMEC (1967); Mallinson (1969); ICI/RoSPA (1970 IS/74); Warren, Lange and Rhynard (1974); Lovstrand (1975); Jowett (1976); J.T. Leonard (1976); G.J. Butterworth (1979a); Denbow and Bright (1979); Felici and Larigaldie (1980); IP (1981 NCSP Pt 3); Cross and Farrer (1982); API (1984 RP 2001, 1991 RP 2003); N. Gibson (1986a); Cross (1987); Kletz (1987d); Luderer (1987); Cartwright (1988); Expert Commission for Safety in the Swiss Chemical Industry (1988); Glor (1988); Mancini (1988); NFPA (1988 NFPA 77); Lüttgens and Glor (1989); Taillet *et al.* (1992)
BS 5958: 1991–

Earthing, grounding (*see* Table 10.2)

Fundamental phenomena
Helmholtz (1879); Lenard (1882); Gouy (1910); Chapman (1913); Stern (1924); Peek (1929); Gemant (1933, 1962); Bikerman (1947); Fröhlich (1949); Butler (1951); Rutgers and de Smet (1952); Meek and Graggs (1953); Klinkenberg (1957, 1964b, 1967c, 1970); Rutgers, de Smet and Myer (1957); Klinkenberg and van der Minne (1958); Pauthenier (1961); Gavis and Hoelscher (1964); D.K. Davies (1967); Douwes and van der Waarden (1967); M.D.Foster (1967); Gavis (1969); Parsons (1971a); Battocletti (1976); Pohl (1978); Gibbings (1979)

Electrical fields
E. Weber (1950, 1965); Friedlander and Reed (1953); Harries (1953); Meek and Graggs (1953); A.D.Moore (1954); W.E. Rogers (1954); Klinkenberg and van der Minne (1958); Moon and Spencer (1961); Vellenga (1961); Carruthers and Wigley (1962); Heidelberg (1970b); Dakin *et al.* (1974); Penman and Fraser (1983)

Electrostatic charging
Coehn (1898); Russel (1909); Loeb (1945, 1958); Holm (1952); Vick (1953); Wagener (1956); Kragelski and Demkin (1960); Harper (1967a,b); D.K. Davies (1970); Gibbings, Saluja and Mackey (1971); Krupp (1971); Bertein (1973); Chives, Mitchel and Rowe (1974); Haenen (1976); Coste and Pechery (1977); Postnikov (1978); Jonassen, Hansson and Nielsen (1979); Cross (1987); Owens (1988); Lüttgens and Glor (1989)

Electrostatic discharge
Heidelberg (1959, 1967, 1970a); Line, Rhodes and Gilmer (1959); Litchfield and Blanc (1959 BM RI 5461); Berz (1961); D.V.Harris, Karel and Ludwig (1961); Bruinzeel (1963); Muller-Hillebrand (1963); N. Gibson and Lloyd (1965); Loeb (1965); J.T. Leonard and Carhart (1967); J.F. Hughes *et al.* (1973); Bertein (1975, 1977); Dorsey (1976); Haig and Bright (1977); J.K. Johnson (1977); Goldman and Goldman (1978); Sigmond (1978); Berta and Gastanek (1979); H. Kramer and Asano (1979); Kalkert and Schecker (1980); Strnad (1980); Glor (1981, 1984, 1988); Guoxiang Li and Wang Changying (1981); Loveland (1981); Lovstrand (1981); Britton and Williams (1982); HSE (1982 OP 5); H.R. Edwards and Underwood (1984); Cross (1987); Glor *et al.* (1987); Maurer *et al.* (1987); Lüttgens and Glor (1989); G.M. Williams and Pratt (1990)

Liquid conductivity
Klinkenberg and van der Minne (1958); Schön (1962a,b, 1965); Douwes and van der Waraden (1967); Klinkenberg (1967a); H. Kramer and Schön (1973, 1975); P.I. Mason (1975); Rees (1975); J.T. Leonard (1976)

Liquid flow in pipes
Mackeown and Wouk (1942); Cooper (1953a); Boumanns (1957); Hampel and Luther (1957); Klinkenberg and van der Minne (1958); Schuringa and Luttik (1960); Gavis and Koszman (1961); Carruthers and Marsh (1962); Gavis (1964, 1967a,b, 1972); Koszman and Gavis (1962a,b); Schön (1962a, 1965); Klinkenberg (1964a,b, 1967b,c, 1971); Vellenga and Klinkenberg (1965); Gibbings and Hignett (1966); Gibbings (1967); N. Gibson and Lloyd (1967, 1970a,b); Schön and Masuda (1967, 1969); Goodfellow and Graydon (1968a,b); J.T. Leonard and Carhart (1970); N. Gibson (1971); Schön and Kramer (1971); Lauer and Antal (1972); Cross, Haig and Cetronio (1977); Touchard (1978); Touchard and Dumarque (1978); P.I. Mason and Rees (1981); Walmsley and Woodford (1981a,b); Abedian and Sonin (1982); Walmsley (1982, 1983a–c); Britton and Smith (1988); Pratt *et al.* (1989); Watanabe *et al.* (1991)
Ball valves: N. Gibson and Lloyd (1975); Kletz (1989e)
Filters: Cooper (1953a); Schön (1965); Gavis and Wagner (1967, 1968); Masuda and Schön (1967); N. Gibson (1969, 1979); J.T. Leonard and Carhart (1970); Huber and Sonin (1975)

Liquid droplets, bubbles, etc.
Lenard (1882); Raleigh (1882); Iribane and Mason (1967); Jonas and Mason (1968); Levin and Hobbs (1971); Schweitzer and Hanson (1971); Vos (1971); Vos, Ramakers and van de Weerd (1974); Napier and Rossell (1977); Felici (1979); H. Kramer (1981); Castle and Inculet (1991)

Liquid droplet settling
von Smoluchowski (1921); Klinkenberg and van der Minne (1958)

Liquid agitation
Vos *et al.* (1974); H. Kramer (1981)

Liquid aerosols, mists and sprays
C.N. Davies (1966); N. Gibson (1971); J.F. Hughes *et al.* (1973); Napier and Rossell (1973); Bassett (1975); Jennings (1975); J.T. Leonard and Clark (1975); G.J. Butterworth and Dowling (1981); Castle, Inculet and Littlewood (1983); Astbury (1991)
Fire extinguishers, including carbon dioxide: Heidelberg, Nabert and Schön (1958a,b); Haessler (1963); Schön and Masuda (1969); Cockram (1971); J.T. Leonard and Clark (1977); Butterworth (1979b); Anon. (1980j); Collocot, Morgan and Morrow (1980); V.T. Morgan, Collocott and Morrow (1981)
Steam, including steam curtains: Napier (1974a); Anon. (1978 LPB 21, p. 81)

Liquid foams
Howells (1993 LPB 114)

Behaviour of chemicals
Ethyl acetate: Bond (1994 LPB 119)

Tanks, vessels, including filling
Heidelberg and Schon (1961); Vellenga (1961); Carruthers and Wigley (1962); Bruinzeel (1963); Bustin, Koszman and Tobye (1964); Vellenga and Klinkenberg (1965); M.D. Foster (1967); J.T. Leonard and Carhart (1967); Tinson (1967); Bulkley and Ginsburgh (1968); Schön and Masuda (1969); H. Kramer and Schön (1973, 1975); Diserens, Smith and Bright (1975); Asano, Kramer and Schön (1977); Bright and Haig (1977); P. Lees *et al.* (1981); G.J. Butterworth and Brown (1982); Matsubara (1991); Pratt (1992)

Road and rail tankers, including filling
OIA (Publ. 711); D.V. Harris, Karel and Ludwig (1961); Herzog, Ballard and Hartung (1961, 1964); L. Wright and Ginsburgh (1963); Holdsworth, van der Minne and Vellenga (1964); Bulkley and Ginsburgh (1968); Mahley and Warren (1968); Lyle and Strawson (1971, 1972, 1973); H. Kramer and Schön (1973, 1975); Strawson and Lyle (1975a,b); H. Kramer, Asano and Schön (1977); Rees (1981); Anon. (1990 LPB 95, p. 5)

Intermediate bulk containers
Ebadat and Cartwright (1991a,b); Britton (1993); Dahn, Kushani and Reyes (1994)

Drums
Pesetsky and Fisher (1975); Britton and Smith (1988); Rosenthal (1988)

Tankers, including tank cleaning
Holdsworth *et al.* (1962); Bustin (1963, 1973–74); Rees (1971); van der Meer (1971); Smit (1971); Vos (1971); van de Weerd (1971, 1972, 1975); J.F. Hughes *et al.* (1973); A.W. Bright and Hughes (1975); H.R. Edwards (1983); J.S. Mills and Haighton (1983); J.S. Mills and Oldham (1983); M.R.O. Jones and Bond (1984, 1985); Anon. (1994 LPB 118, p. 14)

Powders and dusts
Boyle and Llewellyn (1950a,b); Müller-Hildebrand (1963); N. Gibson (1969, 1970, 1972, 1973b); Lapple (1970); Ramackers (1970); Eden (1971, 1972); A.W. Bright (1977); Blythe and Reddish (1979); Lloyd (1979); Anon. (1980 LPB 35, p. 1); Boschung and Glor (1980); Napier (1983); Glor (1984, 1985, 1987, 1988); Maurer (1984); T.B. Jones (1987); Ebadat (1991, 1993); Wolfson Electrostatic Unit (1991); Britton (1993)
Powder flow in pipes: Cole, Baum and Mobbs (1969–70); van de Weerd (1974); Masuda, Komatsu and Iinoya (1976); Boschung and Glor (1980); Napier (1983); Touchard *et al.* (1987); Bond (1989 LPB 88); Dahn (1992)
Silos: J.F. Hughes *et al.* (1975); Blythe and Reddish (1979); Maurer (1979); Britton (1988); Glor (1988)

Containment and containment materials
Keller and Hoelscher (1957); Heidelberg and Schön (1960); Heidelberg (1970a,b, 1971); N. Gibson and Harper (1981a)

Belts, conveyors
Bulgin (1945); Hubbard (1967, 1971a); Cunningham (1970); Javadi and Napier (1974)

Human body
Bulgin (1945); P.S.H. Henry (1971a); L.G. Wilson and Cavanagh (1972); Movilliat and Monomakoff (1977); N. Wilson (1977, 1979, 1983); Greason (1979); Movilliat and Giltaire (1979); Tolson (1980); R.W. Johnson (1981); Berkey, Pratt and Williams (1988); Bailey, Smallwood and Tomita (1991)

Humidity
Smail, Brooksbank and Thornton (1931)

Aircraft systems
Winter (1962); Bruinzeel (1963); D.V. Harris, Karel and Ludwig (1967); Tinson (1967)

Measurements
M.D. Foster and Marsh (1964); Beck *et al.* (1971); Cross (1987); Lüttgens and Glor (1989)

There are also industrial processes in which static electricity is exploited. They include electrostatic gas filtration and electrostatic spray coating. An account of these processes, which are of minimal interest here, is given by Cross (1987).

Static electricity is essentially a phenomenon of low current but high voltage. A low conductivity liquid flowing through a pipeline can generate charge at a rate of 10^{-9}–10^{-6} A. A powder coming out of a grinding

Table 16.33 *Some systems in the process industries where static electricity effects are important*

System	
Liquid–solid	Flow of liquid through pipes, filters
	Splash filling of tanks
Liquid–liquid	Mixing of immiscible liquids
	Settling of drops of one liquid through another
Gas–liquid	Cleaning with wet steam
	Spraying with water
	Leakage of wet steam
Gas–solid	Pneumatic conveying
	Fluidized beds
Solid–solid	Belt drives
	Conveyor belts
	Reeling of paper or plastics
	Human body

mill can carry charge at a rate of 10^{-8}–10^{-4} A. At a charging rate of 10^{-6} A the potential of a container insulated from earth can rise at a rate of 1000 V/s. Potentials of 10 000 V or more are readily obtained in this way.

Objects which can become charged include process materials, process plant and the human body. As long as any of these can remain charged, the electrostatic hazard is not eliminated.

The static charge may discharge causing an incendive spark or it may give a less hazardous corona discharge or may leak away to earth. Sparks from good conductors are more incendive than are those from poor conductors.

The hazard of static electricity may be estimated by comparing the energy of an electrostatic charge with the minimum ignition energy of flammable gas mixtures and powder or dust suspensions.

Static electricity is a complex phenomenon and it is emphasized that only an outline treatment is given here.

16.7.2 Static ignition incidents

In the past there has often been a tendency in incident investigation where the ignition source could not be identified to ascribe ignition to static electricity. Static is now much better understood and this practice is now less common.

In 1954, a large storage tank at the Shell refinery at Pernis in the Netherlands exploded 40 minutes after the start of pumping of tops naphtha into straight-run naphtha. The fire was quickly put out. Next day a further attempt was made to blend the materials and again an explosion occurred 40 minutes after the start of pumping. The cause of these incidents was determined as static charging of the liquid flowing into the tank and incendive discharge in the tank. These incidents led to a major programme of work by Shell on static electricity.

An explosion occurred in 1956 on the *Esso Paterson* during loading at Baytown, Texas, the ignition being attributed to static electricity.

In 1969, severe explosions occurred on three of Shell's very large crude carriers (VLCCs): the *Marpesa*, which sank, the *Mactra* and the *King Haakon VII*. In all three cases tanks were being cleaned by washing with high pressure water jets, and static electricity generated by the process was identified as the ignition source. Following this set of incidents Shell initiated an extensive programme of work on static electricity in tanker cleaning.

Explosions due to static ignition occur from time to time in the filling of liquid containers, whether storage tanks, road and rail tanks or drums, with hydrocarbon and other flammable liquids.

Explosions have also occurred due to generation of static charge by the discharge of carbon dioxide fire protection systems. Such a discharge caused an explosion in a large storage tank at Biburg in Germany in 1953, which killed 29 people. Another incident involving a carbon dioxide discharge occurred in 1966 on the tanker *Alva Cape*.

The majority of incidents have occurred in earthed containers. Earthing alone does not eliminate the hazard of static electricity.

These incidents are sufficient to indicate the importance of static electricity as an ignition source. Further incidents attributed to static electricity are described in Case Histories B36, B56 and B61.

16.7.3 Some basic relations

In work on static electricity it is often necessary to distinguish between the potential ϕ at a point and the potential difference, or voltage, V between two points. Where one point is earthed and the other is not, the potential and the voltage are the same.

Some of the fundamental relations of static electricity are as follows.

Ohm's law

Ohm's law states that

$$V = IR \qquad [16.7.1]$$

where I is the current (A), R is the resistance (Ω), and V is the potential difference, or voltage (V).

Definitions

The following relations are effectively definitions:

$$R = \frac{V}{I} \qquad [16.7.2]$$

$$G = 1/R \qquad [16.7.3]$$

$$\rho = \frac{RA}{l} \qquad [16.7.4]$$

$$\kappa = l/\rho \qquad [16.7.5]$$

$$C = \frac{q}{V} \qquad [16.7.6]$$

$$\sigma = \frac{q}{A} \qquad [16.7.7]$$

$$s = \frac{q}{V_{\mathrm{cn}}} \qquad [16.7.8]$$

$$\epsilon = \frac{\epsilon_{\mathrm{a}}}{\epsilon_{\mathrm{o}}} \qquad [16.7.9]$$

where A is the area (m^2), C is the capacitance (F), G is the conductance (S), l is the length (m), q is the charge (C), s is the space charge density (C/m^3), V_{cn} is the volume of the containment (m^3), ϵ is the relative permittivity, or dielectric constant, ϵ_a is the absolute permittivity (F/m), ϵ_o is the permittivity of free space (F/m), κ is the conductivity (S/m), ρ is the volume resistivity (Ω m) and σ is the surface charge density (C/m^2). The volume resistivity ρ is frequently referred to simply as the resistivity.

Field strength and force

The field strength E is defined as

$$E = -\frac{dV}{dx} \quad [16.7.10]$$

or

$$E = -\frac{V}{x} \quad [16.7.11]$$

where E is field strength (V/m) and x is the distance (m). Frequently the negative sign in Equation 16.7.11 is dropped, since it is only the magnitude of the voltage or field strength which is of interest.

The force F_e on a body due to the charge on it and to the field in which it is placed is

$$F_e = qE \quad [16.7.12]$$

where F_e is force (N). For a gravitational field

$$mg = qE \quad [16.7.13]$$

where g is the acceleration due to gravity (m/s^2) and m is the mass of the body (kg).

Charge, energy and work

The charge accumulated on a body charged by a current is

$$\frac{dq}{dt} = I \quad [16.7.14]$$

The energy W on a charged body is

$$\frac{dW}{dq} = V \quad [16.7.15]$$

$$= \frac{q}{C} \quad [16.7.16]$$

where W is work, or energy (J).

Then, integrating Equation 16.7.16,

$$W = \frac{1}{2}\frac{q^2}{C} \quad [16.7.17]$$

$$= \frac{1}{2}qV \quad [16.7.18]$$

$$= \frac{1}{2}CV^2 \quad [16.7.19]$$

Equation 16.7.19 also gives the energy of discharge when there is discharge of the full charge on a charged body. If there is a partial discharge from potential V_1 to potential V_2, the energy of discharge is

$$W = \tfrac{1}{2}C(V_1^2 - V_2^2) \quad [16.7.20]$$

Surface charge density and displacement

The surface charge density σ is proportional to the field strength E. For a unidirectional field

$$\sigma \propto E \quad [16.7.21a]$$

$$= \epsilon_a E \quad [16.7.21b]$$

$$= \epsilon\epsilon_o E \quad [16.7.22]$$

For a bidirectional field

$$\sigma = \epsilon_1\epsilon_o E_1 + \epsilon_2\epsilon_o E_2 \quad [16.7.23]$$

where subscripts 1 and 2 denote the two fields.

Another quantity which is used is the displacement D which is defined as

$$|D| = \sigma \quad [16.7.24]$$

Then

$$D \propto E \quad [16.7.25a]$$

$$= \epsilon_a E \quad [16.7.25b]$$

$$= \epsilon\epsilon_o E \quad [16.7.26]$$

where D is the displacement (C/m^2).

Time constant

The time constant for charging and discharge of a liquid is

$$\tau = \frac{\epsilon\epsilon_o}{\kappa} \quad [16.7.27]$$

$$= \epsilon\epsilon_o\rho \quad [16.7.28]$$

where τ is the time constant (s).

16.7.4 Laws of Coulomb, Gauss and Poisson

Coulomb's law

It was shown by Coulomb that the force between two charged bodies is proportional to each of the charges on the two bodies and inversely proportional to the square of the distance between them. In electrostatic units:

$$F_e = \frac{qq'}{x^2} \quad [16.7.29]$$

where q is the charge on one of the bodies (C), q' is the charge on the other body (C) and x is the distance between them (m).

In SI units

$$F_e = \frac{qq'}{4\pi\epsilon\epsilon_o x^2} \quad [16.7.30]$$

where F_e is the force (N), q is the charge on one of the bodies (C), and q' is the charge on the other body (C).

Coulomb's law was originally derived by experiment, but has subsequently been demonstrated theoretically.

It follows from Equations 16.7.12 and 16.7.30 that

$$E = \frac{q'}{4\pi\epsilon\epsilon_o x^2} \quad [16.7.31]$$

Gauss' law

Gauss' law may be stated as

$$\nabla D = s \quad [16.7.32]$$

which in Cartesian co-ordinates becomes

$$\frac{\partial V}{\partial x}+\frac{\partial V}{\partial y}+\frac{\partial V}{\partial z}=s \qquad [16.7.33]$$

where x, y and z are the spatial co-ordinates (m).

It may also be written for a cloud surface S as

$$\int D\,\mathrm{d}S=\Sigma q \qquad [16.7.34]$$

or, from Equations 16.7.26 and 16.7.34,

$$\int E\,\mathrm{d}S=\frac{\Sigma q}{\epsilon\epsilon_0} \qquad [16.7.35]$$

or for constant E

$$ES=\frac{\Sigma q}{\epsilon\epsilon_0} \qquad [16.7.36]$$

Whereas Coulomb's law applies to a point source, Gauss' law is more widely applicable. It is used particularly to estimate capacitance and charge, given the limiting breakdown field strength of air. Several applications of Gauss' law are given below.

Poisson's law

Poisson's law, or equation, is

$$\nabla^2 V=-\frac{s}{\epsilon\epsilon_0} \qquad [16.7.37]$$

which in Cartesian co-ordinates becomes

$$\frac{\partial^2 V}{\partial x^2}+\frac{\partial^2 V}{\partial y^2}+\frac{\partial^2 V}{\partial z^2}=-\frac{s}{\epsilon\epsilon_0} \qquad [16.7.38]$$

In general, applications of Poisson's equation tend to be relatively complex and often involve numerical solution. However, some applications of the equation are given below.

The laws of Coulomb, Gauss and Poisson are all formulations of the same physical law. They relate the charge, the potential and the field strength.

16.7.5 Charge

The charge on a body is expressed as the total charge q, the surface charge density σ or the space charge density s.

Sphere (uniform surface charge density)

For a sphere with uniform surface charge density the charge is

$$q=4\pi a^2\sigma \qquad [16.7.39]$$

where a is the radius of the sphere (m).

Sphere (uniform space charge density)

For a sphere with uniform space charge density the charge is

$$q=\tfrac{4}{3}\pi a^3 s \qquad [16.7.40]$$

Cylinder (uniform space charge density)

For a cylinder with uniform space charge density the charge per unit length is

$$q=\pi r^2 s \qquad [16.7.41]$$

Maximum surface charge

From Gauss' law, as given by Equation 16.7.36, and from Equation 16.7.22, the maximum surface charge on an insulating surface is

$$\sigma_{\max}=\epsilon\epsilon_0 E_\mathrm{b}$$

$$=2.64\times10^{-5}\ \mathrm{C/m^2}$$

where E_b is the breakdown field strength (V/m)

16.7.6 Capacitance

Given the charge on a body, the field strength, potential and capacitance may be obtained from Equations 16.7.6, 16.7.11 and 16.7.22. In this section the general approach to the determination of the capacitance of a system is illustrated for the cases of parallel plates and an isolated sphere and expressions are given for the capacitance of some other common systems. The capacitance of some common objects is also given. Field strengths are treated in the following section.

Parallel plates

For the capacitance of two parallel plates, Equation 16.7.22 yields

$$q=\epsilon\epsilon_0 AE \qquad [16.7.42]$$

and Equation 16.7.10 yields

$$V=Ex \qquad [16.7.43]$$

where A is the area of each plate ($\mathrm{m^2}$) and x is the distance between the plates (m). Combining Equations 16.7.42 and 16.7.43

$$q=CV \qquad [16.7.44]$$

with

$$C=\frac{\epsilon\epsilon_0 A}{x} \qquad [16.7.45]$$

Isolated sphere

For the capacitance of an isolated sphere, Equation 16.7.22 yields

$$q=4\pi r^2\epsilon\epsilon_0 E \qquad [16.7.46]$$

and Equation 16.7.10 yields

$$V=-\int_\infty^a E\,\mathrm{d}r \qquad [16.7.47]$$

where r is the radial distance (m).

Hence, substituting for E in Equation 16.7.47 and integrating gives

$$q=CV \qquad [16.7.48]$$

with

$$C=4\pi\epsilon\epsilon_0 a \qquad [16.7.49]$$

Concentric spheres

The capacitance of two concentric spheres is

$$C=4\pi\epsilon\epsilon_0\frac{ab}{b-a} \qquad [16.7.50]$$

where a and b are the radii of the smaller and larger spheres (m), respectively.

Table 16.34 *The capacitance of some selected objects*[a]

Object	*Capacitance*[b] (pF)
Single bolt	1
Tools	5
Small metal item (scoop, hose nozzle)	10–20
Flange (100 mm nominal)	12 (10–15)
Shovel	20
Small container (bucket, 50 l drum)	20 (10–100)
Medium container (250–500 l)	30–300
General plant item[c]	100–1000
Road tanker	1000
Human body	200 (100–300)

[a] Sources: N. Gibson (1969); BS 5958: Part 1: 1980; Expert Commission (1988); Glor (1988); Lüttgens and Glor (1989).
[b] Approximate values.
[c] Item immediately surrounded by earthed structure.

Sphere and plane
The capacitance of a sphere adjacent to a plane is

$$C = 4\pi\epsilon\epsilon_o a[\psi + 0.5\ln(2a/z)] \qquad [16.7.51]$$

where z is the distance from the nearest point on the sphere to the plane (m) and ψ is Euler's constant. The value of Euler's constant is 0.577.

This system was originally studied by Russel (1909) and is treated by Cross (1987).

Coaxial cylinders
The capacitance of two coaxial cylinders is

$$C = \frac{\epsilon\epsilon_o 2\pi l}{\ln(r_2/r_1)} \qquad [16.7.52]$$

where l is the length of the cylinders (m) and r_1 and r_2 are the radii of the inner and outer cylinders (m), respectively.

Parallel cylinders
The capacitance of two parallel cylinders is

$$C = \frac{\pi\epsilon\epsilon_o l}{\ln\left[\dfrac{a + (a^2 - r^2)^{\frac{1}{2}}}{r}\right]} \qquad [16.7.53]$$

where a is the half-distance between the axes of the cylinders (m) and r is the radius of each cylinder (m).

Common objects
The capacitance of some common objects is given in Table 16.34.

16.7.7 Field strength and breakdown

Permittivity
The permittivity of a substance or medium is generally expressed in terms of its relation to the permittivity of free space. The relative permittivity, or dielectric constant, ϵ of a substance is the ratio of the absolute permittivity of that substance ϵ_a to the permittivity ϵ_o of free space, as given by Equation 16.7.9. Another notation which is quite widely used is to denote the absolute permittivity of a substance as ϵ and the relative permittivity as ϵ_r.

The permittivity ϵ_o of free space is

$$\epsilon_o = 8.85 \times 10^{-12}\ \mathrm{F/m}$$

The relative permittivity, or dielectric constant, of air is about 1, that of hydrocarbons about 2, and that of water about 80.

Parallel plates
From Equation 16.7.42 the field strength between two parallel plates with one at potential V and the other at zero potential is

$$E = \frac{q}{\epsilon\epsilon_o A} \qquad [16.7.54]$$

where A is the area of each plate (m^2).

Isolated sphere
From Equation 16.7.46 the field strength at the surface of an isolated sphere is

$$E = \frac{q}{4\pi\epsilon\epsilon_o a^2} \qquad [16.7.55]$$

where a is the radius of the sphere (m).

Infinite parallel plates (uniform space charge density)
The maximum field strength between two infinite parallel plates with a uniform charge density between them and with both at zero potential occurs at the boundary and is

$$E = \frac{sx}{\epsilon\epsilon_o} \qquad [16.7.56]$$

where x is the half-distance between the plates (m).

Sphere (uniform space charge density)
The maximum field strength in a sphere with a uniform space charge density and with zero potential at the boundary is

$$E = \frac{sa}{3\epsilon\epsilon_o} \qquad [16.7.57]$$

where a is the radius of the sphere (m).

This equation is often applied to systems which approximate a sphere such as a cubic storage tank.

For a sphere with a uniform space charge density exerting fields both inside and outside the sphere the field strengths are

$$E = \left(\frac{s}{3\epsilon\epsilon_o}\right) r \qquad r \le a \qquad [16.7.58a]$$

$$E = \frac{s}{3\epsilon\epsilon_o}\frac{a^3}{r^2} \qquad r > a \qquad [16.7.58b]$$

where r is the radial distance (m).

It can be shown by Gauss' law that the field strength outside a sphere is the same if the total charge q is (1) concentrated at one point, (2) uniformly distributed in space in the sphere and (3) uniformly distributed over the surface of the sphere.

The relation between the field strength and the potential on a sphere is as follows. From Equation 16.7.10, for the sphere

$$V = \int_a^\infty E\, dr \qquad [16.7.59]$$

Then from Equations 16.7.40, 16.7.58 and 16.7.59

$$E = V/a \qquad [16.7.60]$$

Cylinder (uniform space charge density)

The maximum field strength in an infinite cylinder with a uniform space charge density and with zero potential at the boundary is

$$E = \frac{s r_c}{2\epsilon\epsilon_o} \qquad [16.7.61]$$

where r_c is the radius of the cylinder (m). This equation is often applied to pipes.

For a cylinder with a uniform space charge density exerting fields both inside and outside the cylinder the fields strengths are

$$E = \left(\frac{s}{2\epsilon\epsilon_o}\right) r \qquad r \le r_c \qquad [16.7.62a]$$

$$E = \frac{s}{2\epsilon\epsilon_o}\frac{r_c^2}{r} \qquad r \ge r_c \qquad [16.7.62b]$$

Coaxial cylinders (uniform space charge density)

The field strengths at the surfaces of the inner and outer cylinders in a system of two coaxial cylinders with a uniform charge density in the space between them are, respectively

$$E_i = \frac{s r_o}{4\epsilon\epsilon_o}\left[2B + \frac{1 - B^2}{B \ln B}\right] \qquad [16.7.63]$$

$$E_o = \frac{s r_o}{4\epsilon\epsilon_o}\left[2 + \frac{1 - B^2}{B \ln B}\right] \qquad [16.7.64]$$

with

$$B = r_i/r_o \qquad [16.7.65]$$

where E_i and E_o are the field strengths at the surfaces of the inner and outer cylinders (V/m) and r_i and r_o are the radii of the inner and outer cylinders (m). If $r_i \ll r_o$

$$E_i = \frac{s r_o}{4\epsilon\epsilon_o}\frac{1}{B \ln B} \qquad [16.7.66]$$

$$E_o = \frac{s r_o}{2\epsilon\epsilon_o} \qquad [16.7.67]$$

These equations have been applied to the case of a cable hanging inside a storage tank.

Tanks fully and partially filled

A detailed treatment of the field strengths in fully and partially filled tanks is given by Klinkenberg and van der Minne (1958) and further treatments are described below.

Field breakdown

The breakdown field strength E_b of air at atmospheric pressure is usually given as

$$E_b = 3 \times 10^6 \text{ V/m} = 3000 \text{ kV/m} = 3 \text{ MV/m}$$

In fact, the breakdown field strength is a function of the electrode gap. The following data are given by Klinkenberg and van der Minne for the critical field strength between large parallel electrodes in air at atmospheric pressure:

Electrode gap (mm)	*Critical field strength* (kV/m)
0.6	5220
10	3150
100	2650
Large gap	2240

Figure 16.43 gives the breakdown field strength in air over a somewhat wider range.

According to a relationship usually known as Paschen's law, the breakdown field strength is a function of the product Pl of the pressure P and the gap l, where P is pressure (bar) and l is gap width (m). Figure 16.44 shows the breakdown voltage V for air as a function of Pl. For values of $Pl > 10^{-3}$ bar m, this graph is consistent with a constant breakdown field strength of 3000 kV/m.

16.7.8 Electrostatic charging

The conditions for a significant accumulation of electrostatic charge are that there occurs some process which generates the charge and that any process of charge dissipation is sufficiently slow.

There are a number of mechanisms by which an electrostatic charge can build up. The mechanisms of principal interest here are (1) contact and separation, (2) induction, (3) double layer separation and (4) charge sharing. Other mechanisms include (5) corona charging, (6) diffusion charging, and (7) particle capture.

Most accounts of the generation of static electricity begin with a discussion of the electrostatic phenomena involved in the contact and separation of surfaces, in the first instance solid surfaces. If two different materials are rubbed together, so that there is first contact and then separation of their surfaces, charges build up on the surfaces of the two materials, one material having a charge of one polarity and the other a charge of opposite polarity.

Modern theory, stemming from work on solid state physics, treats electrostatic phenomena in terms of electron transfer. If the temperature of a surface is high enough, electrons are emitted from it. This emission is characterized by the electron work function. The work function is lower in conducting materials and higher in insulating ones.

If the surfaces of two different materials at the same temperature are brought into contact, electron transfer occurs. The material with the lower work function is the donor and that with the higher work function the acceptor. Electrons migrate from the former to the latter, so that the acceptor acquires a negative charge and the donor a positive one. At equilibrium the potential difference due to the difference in the two work functions is equal to that due to the charge transfer. The proportion of electrons transferred is very small, at most eight in a million.

If the two surfaces are then separated, charge separation also occurs. Provided charge dissipation is

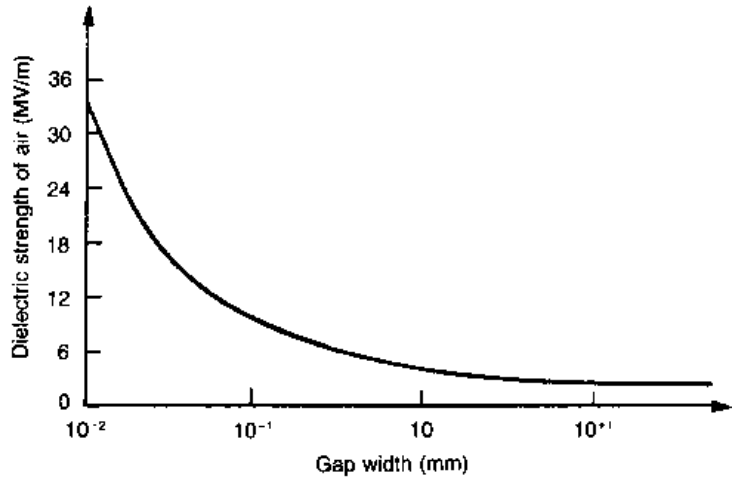


Figure 16.43 *Dielectric strength of air (Glor, 1988): effect of gap width (Courtesy of Research Studies Press)*

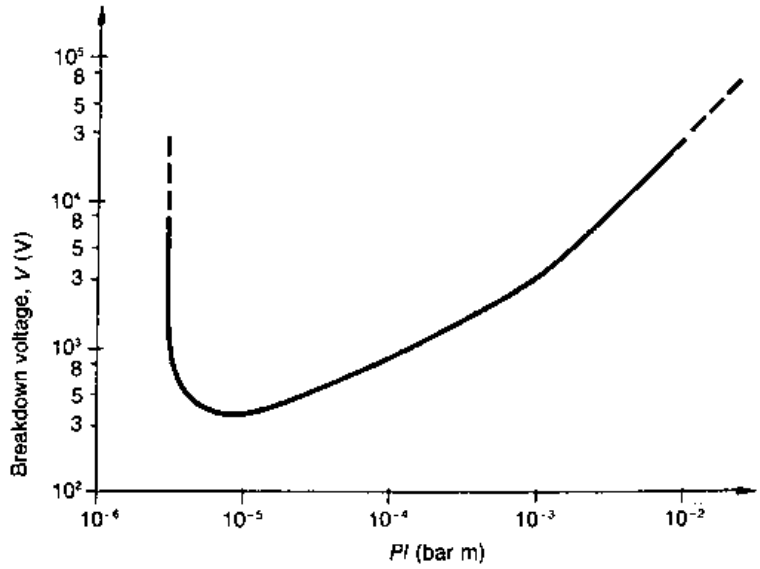


Figure 16.44 *Dielectric strength of air (Glor, 1988): the effect of group Pl (Courtesy of Research Studies Press)*

limited, one material retains a negative charge and the other a positive charge. The two processes of contact and separation comprise the process of charge generation.

Charge is also generated between two surfaces of the same material at different temperatures.

The nature of the charges depends on the permittivity of the two materials. According to Coehn's (1898) 'laws':

(1) the body with the higher permittivity has the positive charge;

(2) the magnitude of the charge is a function of the difference in the permittivities of the two materials.

These 'laws' are, however, controversial. For one thing, as just stated, charge generation can occur between surfaces of the same material.

Materials may be ranked in a triboelectric series. Charge generation is larger for two materials far apart in the series. However, there is no standard triboelectric series, different versions being given by different authorities.

Before separation the distance between the surfaces will be very small, of the order of 10^{-9} m. After separation the capacitance is greatly decreased due to the large increase in the distance between the surfaces. The charge remains constant. The voltage is therefore greatly increased ($q = CV$). The energy is also greatly increased ($W = qV/2$). Energy is supplied to the system as work done in moving the two charges apart.

The model just given is a highly simplified one. In particular, it is based exclusively on electron transfer and takes no account of ion transfer. There are some phenomena which are more readily explained by ion transfer. For example, glass may acquire a negative or a positive charge, depending on whether it has previously been in contact with acid or with alkali. An account of ion transfer is given by Cross (1987).

In discussing charging by contact and separation, Cross draws a distinction between contact and friction charging and states that the failure to distinguish between them has been the cause of much confusion. Friction charging can occur even between identical materials. It is probably a surface temperature effect.

However, some workers prefer to avoid the terms 'contact' and 'friction' altogether. There is no dispute that actual charge accumulation happens when separation occurs, and to this extent the term 'separation charging' may be preferred. Lüttgens and Glor (1989) argue that 'friction charging' is also a misnomer in that charge accumulation has nothing to do with friction *per se*, but is an effect of surface temperature.

Some of the factors which influence the magnitude of charge accumulation in separation charging include (1) the temperature of the surfaces, (2) the permittivity, (3) the number and density of contact points, (4) the electrical conductivity, (5) the speed of separation and (6) changes in the condition of the materials.

The temperature of the surfaces is a fundamental factor determining the extent of electron transfer.

The effect of permittivity is described by Coehn's laws, as already discussed.

The number and density of contact points depends on the force on the two surfaces. Work on a series of metals and polymers has been done by Haenen (1976), who obtained the relation

$$q \propto F_c^n \qquad [16.7.68]$$

where F_c is the force (N/m^2), q is the charge generated (C) and n is an index. The value of n was in the range 0.3–1.0.

The higher the conductivity of the materials, the greater the extent to which any charge generated is neutralized. If both bodies are poor conductors, both will become charged. Of one body is a good conductor and earthed, the charge on that body will flow to earth. If one body is a good conductor but not earthed, the charge will distribute itself over the body. In this way a considerable charge may build up.

The speed of separation is another factor governing the extent of charge neutralization. The higher the speed of separation, the less time there is available for charge neutralization to occur.

Physical changes in the condition of the materials, such as expansion and compression, must have some effect, but are not well documented.

Another important mechanism of charging is induction. Induction charging occurs only where the body is a conductor. If a body which is an isolated conductor is placed in an electrical field, charges of different polarity are induced on opposite sides. If then an earthed electrode touches, or even approaches close to, this body, the charges close to the electrode flow away, leaving the body with a charge of opposite sign.

This effect may be illustrated by the situation shown in Figure 16.45. In Figure 16.45(a) the man, wearing non-conducting footwear approaches a positively charged conveyor belt. A negative charge is induced on the upper part of his body on the side nearer the belt, and a positive charge on the lower part. In Figure 16.45(b) he touches an earthed point on the conveyor and the negative charge leaks to earth. In Figure 16.45(c) he is left with a positive charge which equalizes over his body.

Liquids also can be charged by induction. A charging mechanism which is particularly important for liquids is double layer separation. If an ionic substance is dissolved in a liquid of high dielectric constant, the ions are dissociated and in an electrical field they move in opposite directions. An example of such a situation is sodium chloride ions in water. At an interface such as a pipe wall ions of one charge will be held strongly, whilst those of the other charge will be held less strongly and

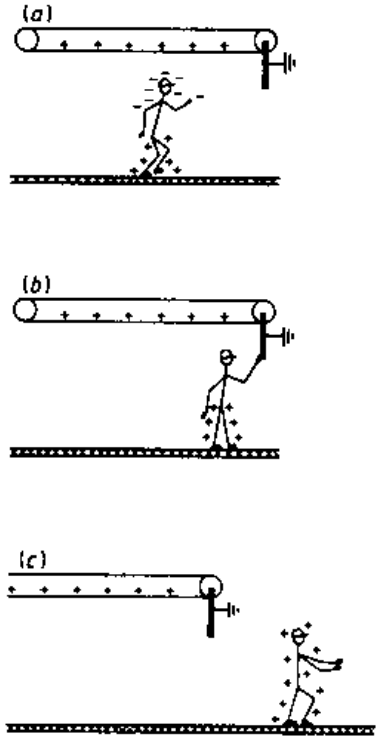


Figure 16.45 *Inductive charging of the human body (Cross, 1987): (a) the charge separates in the field due to the charged belt; (b) the charge from top of the body flows to earth; and (c) the body is left with a net charge (Courtesy of Adam Hilger)*

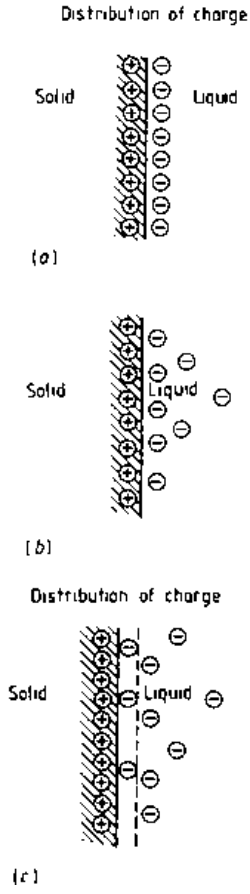


Figure 16.46 *Double layer at a solid–liquid interface (Cross, 1987): (a) Helmholtz model; (b) Gouy–Chapman model; and (c) Stern model (Courtesy of Adam Hilger)*

will form a diffuse layer. For a liquid with conductivity as high as that of water, the diffuse layer will be only a few molecules thick. Liquids such as hydrocarbons, however, also contain some ions. For these liquids, which have much lower conductivity, the diffuse layer will be much thicker.

There are a number of models of the double layer, as shown in Figure 16.46. The original model was that of Helmholtz (1879). In the Helmholtz model, shown in Figure 16.46(a), the layer of counter ions is compact, in the Guoy–Chapman model (Guoy 1910, 1917; Chapman, 1913), shown in Figure 16.46(b) the layer is more diffuse, whilst in the Stern model (Stern, 1924), shown in Figure 16.46(c), the layer of counter ions partly compact and partly diffuse. If the liquid moves through the pipe, the diffuse layer moves with the liquid and charge separation occurs.

Some of the factors which influence the magnitude of charge accumulation in liquid double layer separation include (1) permittivity, (2) electrical conductivity and (3) speed of separation. The effects of these variables are discussed below.

Charge accumulation over time is not necessarily a simple monotonic process. There are three principal patterns of charge accumulation, as shown in Figure 16.47. The charge may either (a) rise to a maximum and stay there, (b) rise to a maximum and then stabilize at a lower plateau, or (c) rise to a maximum, fall to zero and then stabilize at a plateau of opposite sign.

The time taken to reach the maximum value may be characterized by the half-life, which is a function of the materials.

Charge sharing occurs when two bodies, at least one of which is charged, come into contact and charge passes from one to the other. It is relevant particularly to mists and dusts.

Corona charging can be used to create a defined charge on a body for experimental purposes. An account is given by Cross (1987).

Diffusion charging of particles occurs as a result of collisions between particles and ions in a gas.

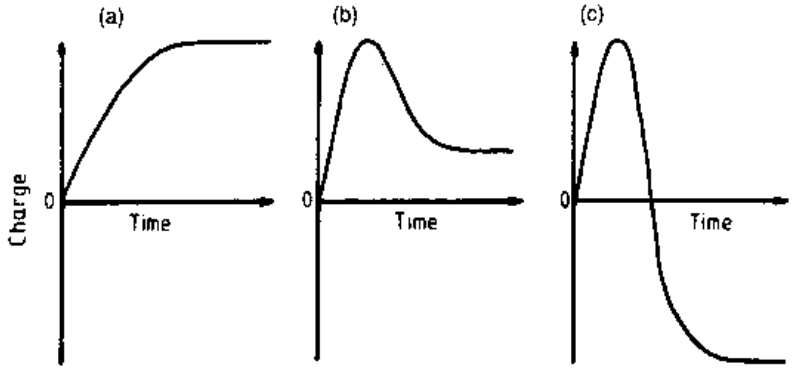


Figure 16.47 *A streaming current in a liquid flowing in a pipe (Cross, 1987; after Coste and Pechery, 1977): (a) monotonic rise; (b) initial peak followed by a fall to a plateau; and (c) initial peak followed by a fall to a plateau, with reversal of sign (Courtesy of Adam Hilger)*

Particle capture, particularly the capture of small particles by larger ones, is another mechanism of charging.

In certain situations it is possible to calculate the limiting charge density. The limiting factor is the charge which gives an electric field strength equal to the breakdown field strength of air. Gauss' law, given below, may be used to determine the limiting surface charge densities and also the limiting volume charge densities.

Little has been said so far about the polarity of the charge. This is important in some applications, as described below.

Processes in which charge separation occurs include: (1) flow of liquids, (2) transfer of liquids, (3) size reduction, (4) transfer of powders, (5) reeling processes and (6) rotation of belts.

16.7.9 Electrostatic charge accumulation, retention and relaxation

The charging processes described lead to an accumulation of charge in the system. In the general case this input of charge is balanced by an output. This output may take various forms. Charge may be carried away in material leaving the system or it may leak away to earth. This situation is commonly represented by the equivalent electrical diagram such as that shown in Figure 16.48.

One common case is where the charging current on an object is balanced by the leakage current so that the system is at steady state. Then the voltage V of the object is then related to the charging current I and the resistance R to earth by Equation 16.7.1 (Ohm's law).

This situation is relevant to earthing. If the charging current is known, it is possible to ensure that the voltage does not exceed a specified limit by ensuring a suitable resistance to earth. The limit on the voltage is generally set in order to avoid an incendive spark. The limiting factor may be the need to avoid a field strength which causes breakdown or the need to avoid an accumulation of energy which equals the minimum ignition energy of the flammable mixture. The energy accumulated also depends on the capacitance of the object. Table 16.35 gives typical electrostatic potentials and spark energies quoted for charged objects.

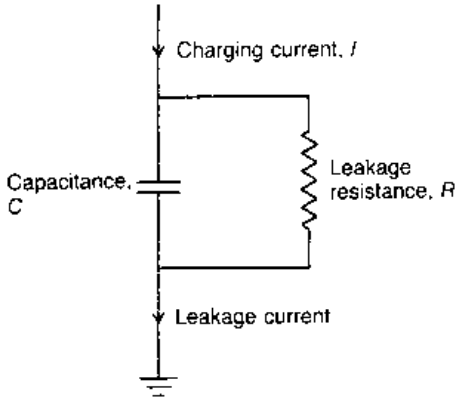


Figure 16.48 *Equivalent electrical circuit for an electrostatically charged conductor (BS 6958: Part 1: 1980) (Courtesy of the British Standards Institution)*

Table 16.35 *Typical electrostatic potentials and spark energies of selected objects*

	Potential (kV)	*Spark energy* (mJ)
Flange	10	0.5
Shovel	15	2
Drum	20	40
Road tanker	15	100
Human body	10	10
Flange on a glass line with toluene flowing in it	≤15	
Flange on a steam ejector	≤15	
Transmission belt (speed 3–15 m/s)	≤80	
Surface of liquid fuel in large container which has been filled rapidly	≤100	

Sources: Britton and Smith (1988); Expert Commission (1988); Glor (1988).

Another common case is where material undergoes a transition from a situation where it was being charged to one where the charging reduces or ceases. It is then able to dissipate this charge, usually by leakage to a containment and so to earth. This process is known as relaxation. It is relevant particularly to liquids. Where a liquid has acquired a charge, arrangements may be made to allow the charge to relax. In a flow system these take the form of providing residence time, whilst in a storage or tanker system they involve allowing time to elapse before operations are undertaken.

Some of the relations commonly used for the charging and discharge of a system are as follows.

Charging of a condenser

The relations for the charging of, and discharge from, a simple resistance–capacitance (RC) circuit provide the basis for analysis of more complex systems. For the charging of such a circuit

$$\frac{dq}{dt} = I \qquad [16.7.69]$$

$$I = \frac{1}{R}(V_o - V) \qquad [16.7.70]$$

From Equations 16.7.6, 16.7.69 and 16.7.70 the unsteady-state charge balance on the capacitance gives

$$\tau \frac{dV}{dt} = V_o - V \qquad [16.7.71]$$

with

$$\tau = RC \qquad [16.7.72]$$

Integrating Equation 16.7.71

$$V = V_o[1 - \exp(-t/\tau)] \qquad [16.7.73]$$

Multiplying Equation 16.7.73 by C and applying Equation 16.7.6

$$q = q_o[1 - \exp(-t/\tau)] \quad [16.7.74]$$

Differentiating Equation 16.7.74 and utilizing Equation 16.7.69

$$I = I_o \exp(-t/\tau) \quad [16.7.75]$$

where I_o is the current at the start of charging (A), q_o is the charge equivalent to the impressed voltage, or the charge at the end of charging (C), and V_o is the voltage across the circuit, or the voltage at the start of charging (V).

Discharge of a condenser

For the discharge of the circuit the unsteady-state charge balance is, from Equations 16.7.1, 16.7.6 and 16.7.69

$$\tau \frac{dV}{dt} = -V \quad [16.7.76]$$

Integrating Equation 16.7.76

$$V = V_o \exp(-t/\tau) \quad [16.7.77]$$

Multiplying Equation 16.7.77 by C and applying Equation 16.7.6

$$q = q_o \exp(-t/\tau) \quad [16.7.78]$$

Differentiating Equation 16.7.78 and utilizing Equation 16.7.69

$$I = I_o \exp(-t/\tau) \quad [16.7.79]$$

Charging of a tank

For the charging of a tank into which liquid is being pumped, from Equation 16.7.4

$$R = \frac{\rho h}{A} \quad [16.7.80a]$$

$$R = \frac{h}{\kappa A} \quad [16.7.80b]$$

where h is the height of liquid in the tank (m). The relationships for the time constant τ are given by Equations 16.7.27, 16.7.72 and 16.7.80.

The initial and final charges in the tank contents are $q = 0$ and $q = q_o$. The initial rate of change of charge is the charge current in the liquid entering the tank, or streaming current I_o:

$$\left(\frac{dq}{dt}\right)_{t=0} = I_o \quad [16.7.81]$$

The unsteady-state charge balance on the tank is

$$\tau \frac{dq}{dt} = q_o - q \quad [16.7.82]$$

From Equations 16.7.81 and 16.7.82

$$q_o = I_o \tau \quad [16.7.83]$$

Integration of Equation 16.7.82 gives, for tank charging, Equation 16.7.74.

Relaxation of a tank

Equation 16.7.78 is applicable for the relaxation of charge in a liquid in a tank into which pumping has just stopped. The rate of decay in this case may be defined in terms of the relaxation time τ or of the charge half-life $t_{\frac{1}{2}}$. The relationship between the two is

$$\frac{t_{\frac{1}{2}}}{\tau} = \ln 2 = 0.693 \quad [16.7.84]$$

where $t_{\frac{1}{2}}$ is the half-life (s). The charge decays during relaxation to 50% of its original value in 0.69τ, 37% in 1τ and 5% in 3τ.

16.7.10 Electrostatic discharge

When an electrostatic charge has accumulated, it may discharge either by leaking away, usually to earth, or by a specific mode of discharge. There are a number of mechanisms by which an electrostatic charge can discharge. Those of principal interest here are (1) spark discharge, (2) brush discharge, (3) corona discharge, (4) propagating brush discharge and (5) bulking brush discharge.

A corona discharge can cause ignition of a flammable gas mixture but its incendivity is borderline; it is sometimes stated to be non-incendive to flammable gases or dusts. Essentially it is incendive only to gases with very low minimum ignition energies such as hydrogen and carbon disulphide. The other modes of discharge can be incendive, except that it has not been demonstrated that a brush discharge can ignite dusts.

A corona discharge occurs over a longer time than a spark discharge and may give a faint glow and a sound of hissing.

Streaming currents for substances such as petroleum products are of the order of 10^{-6}–10^{-5} A. Corona currents can be much larger. The existence of a corona may therefore dissipate the charge due to the streaming current and lead to a lower steady-state electrostatic potential.

In discussion of discharges it is usual to speak of the bodies the surfaces of which act as points of discharge as electrodes. In this sense the human body may act as an electrode.

A spark discharge is one which occurs between two conductors isolated from each other and involves two electrodes. Typically one of the conductors is isolated from earth and the other is earthed. Spark discharges are also called capacitor discharges, since any system of two conductors isolated from each other is effectively a capacitor. A spark discharge can occur between a fixed isolated object and an earthed object. Alternatively, one or even both of the objects may be moving.

If the resistance between the origin of the spark and all other points on the conductor is less than about $10^6\,\Omega$, a spark discharge can occur. The resistance above which such a discharge will not occur cannot be stated with any precision.

The value of the breakdown electric field strength usually quoted for air is that applicable to two parallel plates. If the surfaces are not parallel, the breakdown field strength can be lower. There are numerous industrial situations in which there are two objects in combination which constitute a capacitor and which therefore may have the potential for a spark discharge.

A spark discharge occurs in a fraction of a second and gives a short, sharp, crackling sound.

A brush discharge is one which occurs on a single electrode and the discharge ends in space. The electrode

is an earthed conductor. The electric field may be created by a charged insulator or a charged conductor. Most accounts of brush discharges deal mainly with the former.

Some industrial situations in which a brush discharge can occur are as follows. The earthed conductor may be a fixed metal object, a sampling device or the human body. The charged object may be a plastic pipe, a drum or a bag, a conveyor belt, a flowing liquid or a powder or a cloud of spray or dust.

Where the second object, like the first, is a conductor, a spark discharge is also possible, and brush and spark discharges may be in competition. The nature of the discharge depends on the shape of the objects.

A corona discharge is similar to a brush discharge but occurs where the electrode is more pointed. The radius of curvature limits quoted are >5–50 mm for a brush discharge and <1 mm for a corona discharge. A corona discharge may persist over a long period.

There are a number of situations in which a propagating brush discharge may occur. These are where there is (1) a non-conducting film suspended parallel to a conductor, (2) a non-conducting film on a conductor, or (3) a non-conductor. The situation may be explained by reference to Figure 16.49, where Figure 16.49(a) shows an isolated non-conducting film in free space and Figures 16.49(b) and (c) show the first two cases mentioned; the third case is similar to the second as far as the field is concerned. The strength of the electric fields is proportional to the density of the arrows.

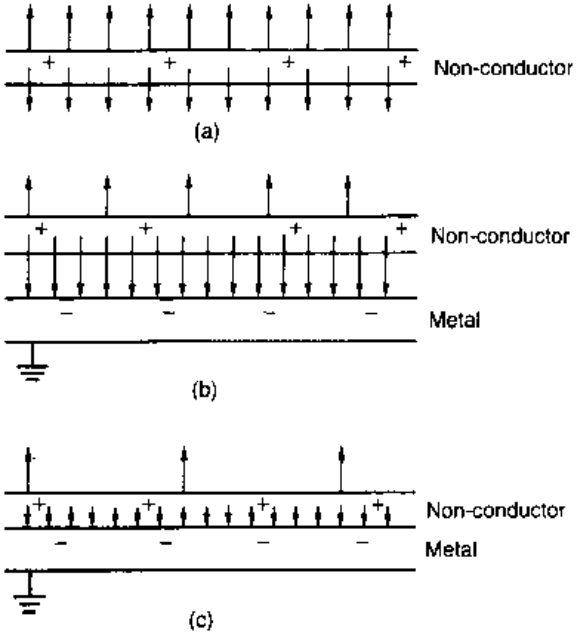


Figure 16.49 *Electric field strength due to an electrically charged sheet (BS 6958: Part 1 1980): (a) isolated sheet; (b) sheet adjacent to a metal plate earthed on the opposite side; and (c) sheet backed by an earthed metal plate (Courtesy of the British Standards Institution)*

For the isolated film in free space the breakdown field strength of air sets a limit on the surface charge density. For case 1 the presence of the earthed conductor causes a redistribution of the field so that much of it is directed towards the conductor. In this situation a much higher charge density can be accommodated before field breakdown occurs. For case 2 even greater redirection occurs and an even greater charge density can be accommodated. Case 3 is similar to case 2 except that now there is a single non-conducting object.

A propagating brush discharge can occur if there is a short circuit between the insulating film and the conductor or, in case 3, between one side and the other of the non-conductor. One way in which this can occur is if the film is perforated by mechanical damage. Alternatively, if an electrode approaches the non-conducting surface the field may be altered so that a brush discharge occurs on the electrode; the central channel may extend to that surface and damage it. In either case the change in direction of the field gives a very high field strength across the surface and ionization occurs, so that the whole non-conducting surface then discharges into the original channel.

A suitable colouring powder may be used to effect visualization of the discharge patterns on the insulator surface. These patterns are characteristic and are called Lichtenberg figures. Propagating brush discharges are referred to as Lichtenberg discharges.

Propagating brush discharges have also been reported on insulating film not backed by a conductor. Although propagating brush discharges have traditionally been explained in terms of a non-conducting film adjacent to or on a conducting surface, the more important practical case is that of a non-conducting envelope such as a pipe or container.

Some industrial situations in which a propagating brush discharge can occur include: the flow of a low conductivity liquid or a powder through a pipe or into a container which is either non-conducting or has an insulating internal coating; and rotation of a conveyor belt with a conductive coating on one side.

A bulking brush discharge is a type of brush discharge which can occur on a heap of powder in a silo. Non-conductive, relatively coarse powders are the most susceptible. The discharge spreads over the surface of the powder, starting at the wall and moving to the centre.

Reference should also be made to lightning-like discharges. These have been observed in the ash and dust clouds over volcanoes and at one time it was supposed that such discharges might occur in industrial operations. There is, however, no evidence of this.

The four types of discharge described, other than bulking brush discharge and lightning discharge, are shown in Figure 16.50.

16.7.11 Liquids

Charge generation

Static electricity effects in liquids may usefully be considered in terms of the classical theory of the electrical double layer at an interface. This has been

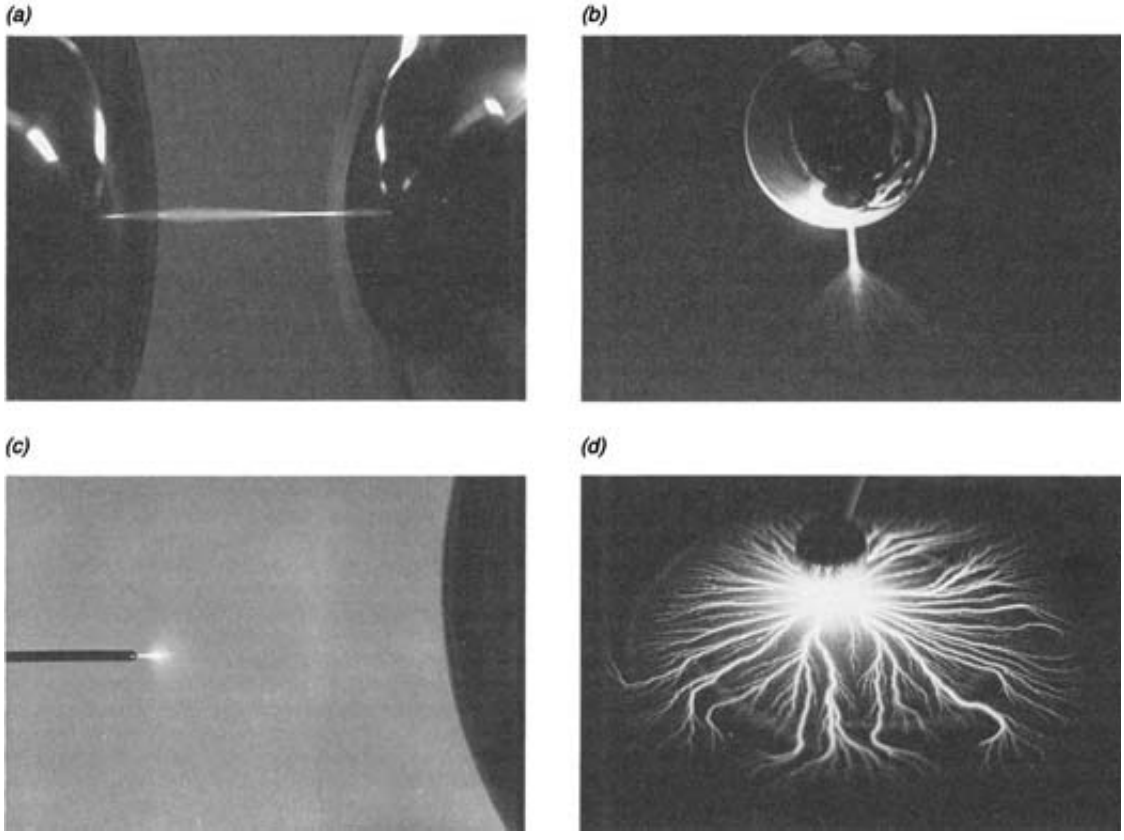


Figure 16.50 *Four types of electrostatic discharge (Lüttgens and Glor, 1989): (a) spark discharge; (b) brush discharge; (c) corona discharge; and (d) propagating brush discharge (Courtesy of Expert Verlag)*

described by Stern as comprising two parts: a compact or Helmholtz layer near the interface and a diffuse or Guoy layer extending further into the liquid.

According to this model, if a liquid such as oil is at rest and in contact with another immiscible liquid such as water or with a solid such as a container wall, there builds up in that liquid an electrical double layer. This electrical double layer may be represented in convenient, though oversimplified, form as one layer of positive ions and one of negative ions. The phenomenon is illustrated schematically in Figures 16.51(a) and (b) for these two cases. There is no significance in the fact that the ions nearest the interface are positive; they could equally well be negative.

If, in the system described, the oil is a poor conductor and there is a relative movement between the surface of the oil and that of the water or of the container, the ions closest to the interface tend to adhere to it so that the oil loses some ions of one particular sign and thus becomes electrostatically charged. Situations in which such charge separation may occur are the pipeline flow of an oil, the settling of water droplets through an oil and the splashing of oil droplets onto the side of a tank, as illustrated in Figures 16.51(c) and (d), (e) and (f), and (g) and (h), respectively.

Some of the situations mentioned are described by the classical electrochemical models. The equations are useful at least as a guide to the factors which are important. In some cases they have been further developed to give relations more applicable to industrial situations.

The extent of charge separation is dependent on the resistivity of the liquid. If its resistivity is low, charge separation is easy, but so is charge recombination through the liquid, while if its resistivity is so high as to be effectively infinite, no charge separation occurs. If the liquid has high resistivity, however, there may be appreciable charge separation without immediate recombination. It is the handling of high resistivity liquids, therefore, which tends to generate static electricity. Examples of low resistivity liquids are water, ethanol and crude oil, and examples of high resistivity liquids are gasoline, kerosene, naphtha, benzene and other white oils.

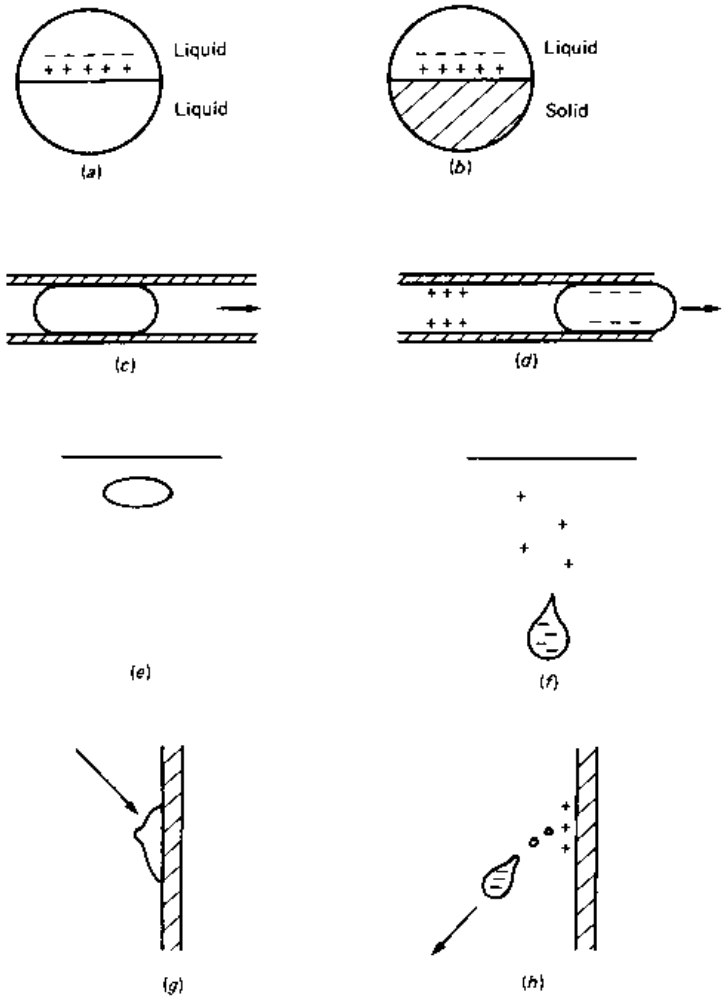


Figure 16.51 *Generation of static electricity in liquid systems: (a) electrical double layer at a liquid–liquid interface; (b) electrical double layer at a liquid–solid interface; (c, d) charge separation as oil flows through a pipeline; (e, f) charge separation as a water drop falls through oil; and (g, h) charge separation as oil splashes onto a tank wall*

Charge discharge

A hazard occurs with a liquid if charge is able to accumulate and if this charge undergoes rapid discharge rather than gradual dissipation. This hazard depends to a large extent on the container in which the liquid is held. Broadly, such containers are (1) containers made of conducting material and earthed, (2) containers made of conducting material and insulated from earth and (3) containers made of non-conducting material.

In process plants the container is usually made of metal and is earthed. If the liquid has low conductivity, it is possible for a large charge to accumulate in the container. The relaxation time for dissipation of the charge may be long. A discharge may occur between the liquid and the earthed container. Thus, in this situation, earthing of the container is not sufficient to eliminate the hazard. The comment has already been made that the majority of ignition incidents have occurred in earthed containers.

It is easier for charge recombination to occur if one, or both, of the two oppositely charged objects is pointed. Thus any metal object which protrudes into a tank and which is electrically connected to it acts as a path for the discharge current. Such an object is known as an 'earthed probe'. Objects which can act as earthed probes include dipsticks and ullage tapes, tank washing machines and metallic objects floating on the liquid surface.

An activity which causes particular risk of discharge is level gauging. If a man standing on a tank inserts a conducting ullage tape into the liquid in the tank and the liquid is charged, a discharge may occur between the liquid and the tape. This may happen in two ways. If the tape is connected to earth via the man, or otherwise, it

can act as an earthed probe. Alternatively, if it is insulated from earth but inserted in the liquid there may be a discharge across to the earthed tank.

A container may be made of metal but insulated from earth. In this case a large charge may accumulate in the liquid and on the container. Then if a path to earth is created there may be a discharge.

A similarly large charge may accumulate in a liquid held in a container made of insulating material, and again discharge may take place if a path to earth occurs.

Another configuration which gives rise to the possibility of discharge is that of an isolated conductor. The conductor may become charged and then give a discharge. Isolated conductors in plant may occur not only in vessels but also in pipework. A section of non-conductive material in metal pipework may constitute an isolated conductor.

If the charged object is a good conductor, it may be treated in the conventional way as an electrical capacitance. The energy available for discharge is given by Equation 16.7.19. The energies calculated in this way may be compared with the minimum ignition energies of flammable gas mixtures and of dust suspensions (as described in Section 16.2 and Chapter 17, respectively) in order to determine the probability that a spark discharge may have sufficient energy to cause ignition.

If the charged object is a poor conductor, no similar calculation of the energy available to produce a spark is possible, because the charge is generally not uniformly distributed and the resistance to its flow is high.

16.7.12 Some electrolytic relations

The model of a hydrocarbon electrolyte which is most often used in work on static electricity is that of a binary, monovalent electrolyte. For such an electrolyte some basic relations are as follows.

The number of charges z is

$$z = |z_+| = |z_-| \qquad [16.7.85]$$

where z is the number of elementary charges per particle.

The ionic mobility u is assumed to be

$$u = u_+ = -u_- \qquad [16.7.86]$$

where u is the ionic mobility ($m^2/V\,s$).

The ionic velocity v is

$$v = uE \qquad [16.7.87]$$

where v is the ionic velocity (m/s).

The charge flux j for each ionic species with concentration n is

$$j = z\frac{n}{N}Fv \qquad [16.7.88]$$

$$j = z\frac{n}{N}FuE \qquad [16.7.89]$$

where F is the charge per kilomole equivalent (C/kmol), j is the charge flux (A/m^2), n is the number of ions per unit volume (ions/m^3), and N is the number of molecules per kilomole (molecules/kmol). F is Faraday's constant ($= 9.65 \times 10^7$) and N is Avogadro's number ($= 6.02 \times 10^{26}$).

The concentration c of each ionic species is

$$c = \frac{n}{N} \qquad [16.7.90]$$

The force F_e due to the electric field is

$$F_e = zeE \qquad [16.7.91]$$

where e is the charge on a proton (C) ($= 1.6 \times 10^{-19}$) and F_e is force (V A s/m).

The electric charge is given by

$$ne = cF \qquad [16.7.92]$$

The total concentration of ions is

$$c_+ + c_- = 2c \qquad [16.7.93]$$

The current density J is

$$J = 2nvze \qquad [16.7.94]$$

$$= 2cvzF \qquad [16.7.95]$$

$$= 2cuzFE \qquad [16.7.96]$$

$$= \kappa E \qquad [16.7.97]$$

with

$$\kappa = 2nuze \qquad [16.7.98]$$

$$= 2cuzF \qquad [16.7.99]$$

where J is the current density (A/m^2). In terms of the ionic concentrations, the conductivity is

$$\kappa = (c_+ + c_-)uF \qquad [16.7.100]$$

where c_+ is the concentration of positive ions (kmol/m^3) and c_- is the concentration of negative ions (kmol/m^3).

The space charge density is

$$s = (c_+ - c_-)F \qquad [16.7.101]$$

The relation between the ionic velocity and the diffusion coefficient is

$$D_m = \frac{kTu}{ze} \qquad [16.7.102]$$

where D_m is the molecular diffusion coefficient (m^2/s), k is Boltzmann's constant ($kg\,m^2/s^2\,K$) and T is the absolute temperature (K).

The relation between the concentration and the conductivity is

$$\kappa_\pm = \frac{c_\pm z^2 F^2 D_m}{RT} \qquad [16.7.103]$$

$$\kappa = \kappa_+ + \kappa_- \qquad [16.7.104]$$

$$\kappa = \frac{(c_+ + c_-)z^2F^2D_m}{RT} \qquad [16.7.105]$$

$$\kappa = \frac{2cz^2F^2D_m}{RT} \qquad [16.7.106]$$

where R is the universal gas constant (kJ/kmol K).

For a liquid from which all the ions of one sign have been removed, Equations 16.7.100 and 16.7.101 become

$$\kappa = cuF \qquad [16.7.107]$$

$$s = cF \qquad [16.7.108]$$

The thickness δ of the double layer is derived as follows. It has been shown by Debye and Huckel that

$$\delta = \left(\frac{\epsilon\epsilon_o kT}{2nz^2e^2}\right)^{\frac{1}{2}} \quad [16.7.109]$$

where k is the Boltzmann constant (J/K) and δ is the thickness of the double layer (m).

From Equations 16.7.98, 16.7.102 and 16.7.109 it can be shown that

$$\delta = (D_m\tau)^{\frac{1}{2}} \quad [16.7.110]$$

The surface charge density σ at the electrical double layer is given by

$$\sigma = \frac{\epsilon\epsilon_o V_d}{\delta} \quad [16.7.111]$$

where V_d is the potential difference across the double layer (V).

Another important parameter is the zeta potential. This is the potential at the plane of slip between the surface and a liquid moving across it. The zeta potential is

$$\zeta = \frac{\eta u}{\epsilon\epsilon_o} \quad [16.7.112]$$

or

$$\zeta = \frac{\eta v}{\epsilon\epsilon_o E} \quad [16.7.113]$$

where ζ is the zeta potential (V) and η is the viscosity of the liquid (kg/m s).

16.7.13 Liquid conductivity

The electrical conductivity of a liquid is due to the presence of ions. This is true for hydrocarbons as well as for aqueous solutions. Addition of ions increases the conductivity and removal of ions decreases it.

It has been found by a number of investigators that the electrical conductivity of hydrocarbon liquids is not a true constant but may vary. It is therefore usual to speak of a 'rest' conductivity, which is the intrinsic property, and an 'effective' conductivity, which depends on the conditions.

Douwes and van der Waarden (1967) showed that when the dc electrical conductivity of hydrocarbons was measured under different conditions so that there were different decay times, extrapolation back to zero time gave conductivities equal to each other and equal to the ac conductivity. They concluded that it was this zero time dc conductivity which is the intrinsic property.

A discussion of fundamental aspects of liquid conductivity has been given by Klinkenberg (1967a).

According to Schön (1967), the effective conductivity κ_e and rest conductivity κ_r (S/m) may vary by a factor of 10. In general, the difference increases as the charge density increases.

Britton and Smith (1988) give relations for the effect of charge density on the conductivity and for the effect of temperature on the effective conductivity. They quote the work of H. Kramer and Schön (1973) on the effect of charge density:

$$\kappa_e = k_1 + k_2 s \quad [16.7.114]$$

where k_1 and k_2 are constants. The constant k_2 is positive for liquids with low rest conductivity ($\leq$1 pS/m) and negative for liquids with a higher rest conductivity. Kramer and Schön obtained a maximum value of 4 for the ratio κ_r/κ_e. For the effect of temperature Britton and Smith quote an equation of P.I. Mason (1975):

$$\log_{10}(\kappa_2/\kappa_1) = k_3(T_2 - T_1) \quad [16.7.115]$$

where k_3 is a constant and subscripts 1 and 2 refer to states 1 and 2, respectively. For liquids such as kerosene, the value of the constant k_3 is about 0.015^oC^{-1}. H. Kramer and Schön (1975) give some experimental data showing the effective conductivity to be, on average, half the rest value. W.D. Rees (1975) reports measurements in which the effective conductivity varied between one-tenth and one-half of the rest value.

The above relations also indicate that for low conductivity liquids the effective conductivity is greater than the rest value. This is important, because the relaxation times for low conductivity liquids are long and any feature which reduces them is helpful. Thus Vellenga and Klinkenberg (1965) have derived a model of charge relaxation in a liquid in which the assumption is that the conductivity is proportional to the charge density, and which gives a hyperbolic rather than an exponential decay. Another model has been given by M.D. Foster (1967).

The range of conductivities which occur in practice is very wide. According to Klinkenberg and van der Minne (1958), the conductivity of a crude oil may be 10^7 times that of a light fraction. There tend to be large differences between the conductivity of pure and commercial chemicals. For example, the conductivity of pure heptane has been given as 0.03 pS/m and that of the commercial product as 10–100 pS/m.

The electrical conductivity, dielectric constant and relaxation time of selected liquids are shown in Table 16.36. Relaxation times vary from very small fractions of a second for some crude oils up to minutes or even hours for some highly purified products.

One broad classification of liquid conductivity (Expert Commission, 1988) is that liquids with a conductivity of less than 10^{-8} S/m are classed as non-conductive and those with a conductivity exceeding this are classed as conductive. Examples quoted of non-conductive liquids are aliphatic and aromatic hydrocarbons, ethers and methane derivatives, and examples of conductive liquids are hydrocarbons with polar groups, alcohols, aldehydes, ketones, acids, esters (except those of higher acids), nitriles, amides, amines and nitro compounds.

Two liquid conductivities which are commonly taken as demarcation values are 1 pS/m and 50 pS/m. A conductivity less than 1 pS/m is commonly classed as very low and one in the range 1–50 pS/m as low. The conductivity criterion of 50 pS/m appears to derive in large part from the work at Shell (e.g. Klinkenberg and van der Minne, 1958). It is quoted as a demarcation value in codes such as NFPA 77: 1988 and BS 5958: 1991.

The greatest danger occurs where the liquid conductivity is in the intermediate range, i.e. not so low that there is little charge generation and not so high that charge equalization is very rapid. Figure 16.52 illustrates the zone of particular hazard.

Mention is made in the literature of the possibility of pro-static agents and of 'hot fluids', but usually only in passing.

Table 16.36 *Electrical conductivity, dielectric constant and relaxation time of selected liquids*

A Electrical conductivity, dielectric constant and relaxation time			
	Electrical conductivity (S/m)	*Dielectric constant*	*Relaxation time* (s)
Highly purified hydrocarbons	10^{-15}	2	1.8×10^{4}
White products	10^{-13}–10^{-10}	2	1.8×10^{-1}–10^{2}
Crude oil	10^{-9}–10^{-7}	2	1.8×10^{-4}–1.8×10^{-2}
Demineralized water	10^{-5}	80	7.1×10^{-5}
B Dielectric constant			
Hexane	1.9		
Heptane	2.0		
Benzene	2.3		
Toluene	2.4		
Cyclohexane	2.0		
Ethyl ether	4.3		
Acetone	21.0		
Methanol	33.7		
Ethanol	25.7		

Sources: Klinkenberg and van der Minne (1958); Eichel (1967); Napier (1971).

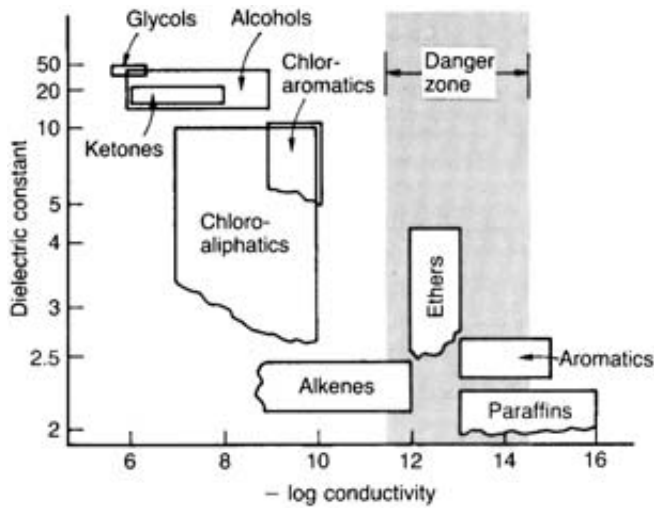


Figure 16.52 *Liquid electrical conductivity (Saletan, 1959b): conductivity ranges of selected liquids (Courtesy of* Chemical Engineering*)*

A note on the units of conductivity/resistivity is given in the notation at the end of this chapter.

16.7.14 Liquid flow in pipes

One of the most important situations in which static electricity may be generated by a liquid is in flow through a pipe into a receiver such as a storage tank or a road or rail tanker. The flow of liquid results in a charging, or streaming, current which then transports charge into the receiver.

Factors which affect the charge generation in liquid flow in pipes include the pipe diameter and material, the liquid viscosity and electrical conductivity, and the liquid velocity. Impurities, including water, are also important.

Figure 16.53, from Leonard and Carhart (1970), illustrates the variation of charging current with conductivity.

The charge generated by a liquid flowing in a pipe is greatly increased if the liquid contains water. An increase in the charge generated by a factor of up to 50 is quoted by Klinkenberg and van der Minne (1958). Many accidents attributed to static electricity have involved wet liquids.

Charge generation by liquid flow in pipes has been modelled by a number of workers and some success has been achieved in explaining theoretically the charging currents generated in small diameter pipes, but there has been less success with large pipes and for these it is

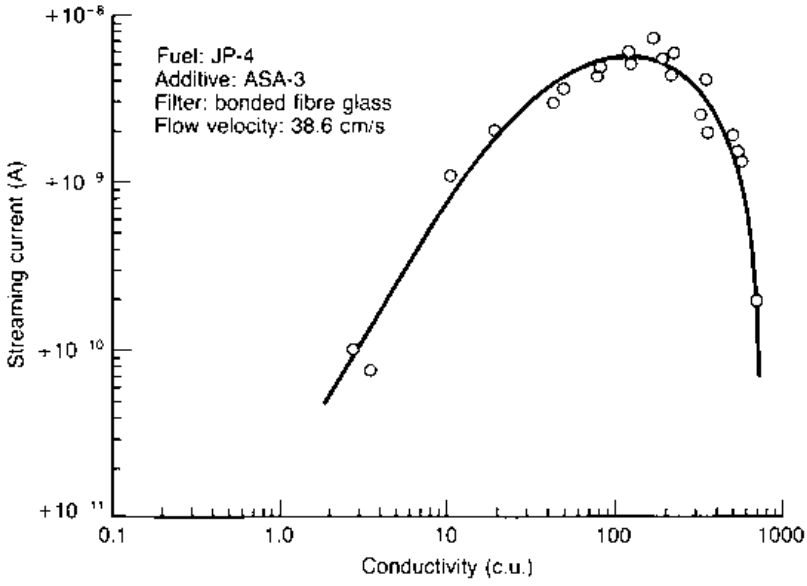


Figure 16.53 *Streaming current for liquid flow in a pipe (Leonard and Carhart, 1970): effect of liquid electrical conductivity (Courtesy of the* Journal of Colloid and Interface Science*)*

necessary to rely on empirical correlations. Empirical correlations are generally of the form

$$I \propto u^m d^n \qquad [16.7.116]$$

where d is the pipe diameter (m), I is the streaming current (A), u is the velocity of the liquid (m/s) and m and n are indices.

Most of the work on liquid flow in pipes refers to metal pipes, but there is a limited amount of work on non-conducting pipes. Obstructions in the pipe may cause appreciable charge generation. Filters are the main case in point, but other items such as ball valves have also received attention.

16.7.15 Early models

Early theories of charge generation by a liquid flowing in a pipe were given by W.F. Cooper (1953a) and Boumanns (1957). In Boumanns' theory charge is generated as the flow of liquid entrains ions from the double layer. But this mechanism, whilst capable of giving a transient, does not fully explain the existence of a steady-state current. Boumans therefore introduced the concept of a 'wall current'.

Another early model was that of Schön, given in unpublished work quoted by Hampel and Luther (1957). This work is also referred to by Klinkenberg and van der Minne (1958).

16.7.16 Klinkenberg and van der Minne model

A model for the streaming current and the streaming potential for the flow of liquid in a pipe has been given by Klinkenberg and van der Minne (1958). The assumptions of the model are that (a) the electrical double layer is thin compared with the pipe diameter, (b) this layer is also thin compared with the laminar sublayer, (c) the streaming current is independent of the pipe length, and (d) the shear stress is constant throughout the electrical double layer.

The charging current I is

$$I = \pi d_p \int s v \mathrm{d}x \qquad [16.7.117]$$

where d_p is the pipe diameter (m) and x is the distance from the pipe wall (m).

The shear stress τ_s in the electrical double layer is

$$\tau_s = \eta \frac{\mathrm{d}v}{\mathrm{d}x} \qquad [16.7.118]$$

where η is the viscosity of the liquid (kg/m s) and τ_s is the shear stress (N/m^2). Then, since the shear stress is assumed constant throughout the layer,

$$\tau_{so} = \frac{\eta v}{x} \qquad [16.7.119]$$

where τ_{so} is the shear stress at the wall (N/m^2).

Applying Poisson's equation, Equation 16.7.38, in one dimension

$$s = -\epsilon\epsilon_o \frac{\mathrm{d}^2 V}{\mathrm{d}x^2} \qquad [16.7.120]$$

Hence from Equations 16.7.117–16.7.120

$$I = -\frac{\pi d_p \tau_{so} \epsilon\epsilon_o}{\eta} \int x \frac{\mathrm{d}^2 V}{\mathrm{d}x^2}\, \mathrm{d}x \qquad [16.7.121]$$

Integrating Equation 16.7.121 between the wall ($x = 0$) and the plane where the potential gradient is zero ($dV/dx = 0$)

$$I = -\frac{\pi d_p \tau_{so} \epsilon \epsilon_o}{\eta} \left(x \frac{dV}{dx} - \int \frac{dV}{dx}\, dx \right)_{x=0}^{dV/dx=0} \quad [16.7.122]$$

For the limit just given the first term in the integration in Equation 16.7.122 is zero. The second term may be replaced by the zeta potential. Hence

$$I = -\frac{\pi d_p \tau_{so} \epsilon \epsilon_o \zeta}{\eta} \quad [16.7.123]$$

Eliminating the shear stress by using a force balance which introduces the pressure drop

$$\pi d_p l \tau_{so} = A_p \Delta P \quad [16.7.124]$$

where A_p is the pipe cross-sectional area (m^2), l is the pipe length (m) and ΔP is the pressure drop (N/m^2).

Hence from Equations 16.7.123 and 16.7.124

$$I = -\frac{A_p}{l} \frac{\epsilon \epsilon_o \zeta}{\eta} \Delta P \quad [16.7.125]$$

The streaming potential V_s is obtained by equating the streaming current to minus the leakage current through the liquid in the pipe:

$$I = -\frac{V_s}{R_p} \quad [16.7.126]$$

where R_p is the resistance of the liquid in the pipe (Ω) and V_s is the streaming potential (V). Then from Equations 16.7.4, 16.7.5 and 16.7.126

$$I = -\frac{A_p \kappa}{l} V_s \quad [16.7.127]$$

Equating Equations 16.7.125 and 16.7.127 yields

$$V_s = \frac{\epsilon \epsilon_o \zeta}{\kappa \eta} \Delta P \quad [16.7.128]$$

16.7.17 Koszman and Gavis model

Another theoretical model, or rather suite of models, is that of Koszman and Gavis (Gavis and Koszman, 1961; Koszman and Gavis, 1962a,b). They postulate that electrolytic oxidation–reduction reactions can occur in hydrocarbons, that in effect a cell reaction occurs in the pipe, and that the current flow is associated with this reaction. With current flow, concentration polarization will occur. They thus avoid the need to assume a wall current of unspecified origin. The current is explicitly described as a diffusion current due to the concentration polarization. The Koszman and Gavis models are given in cgs units and these units are retained for these models here.

The first model derived is for a low conductivity liquid. The mechanisms of charge transport are diffusion, convection and electrical conduction. The basic equation for charge transport, or current, is

$$I = -D_m \nabla q - \kappa \nabla \phi + vq \quad [16.7.129]$$

where D_m is the diffusion coefficient (cm^2/s), I is the streaming current (A), q is the charge (C), v is the local velocity (cm/s), κ is the electrical conductivity of the liquid ($\Omega^{-1}\,cm^{-1}$) and ϕ is the potential (V). The solution of the charging current equation is

$$I = \frac{2\pi r_p u D_m \tau F (c_o - c_s)}{\delta_m n_t} [1 - \exp(-L/u\tau)] \quad [16.7.130]$$

where c_o is the concentration of the discharging ion in the bulk fluid (mol/cm^3), c_s is the concentration of the discharging ion at the pipe wall (mol/cm^3), F is Faraday's constant ($= 96\,500$ C/mol), L is the length of tube (cm), n_t is the transference number, r_p is the pipe radius (cm), u is the average velocity (cm/s), δ_m is the thickness of the diffusion layer (cm) and τ the relaxation time (s).

The total transport of charge across the diffusion layer includes normal conduction transport under the influence of the potential difference between the tube and the bulk liquid, and it is therefore necessary to include the transference number n_t of the ions of charge opposite to those being discharged.

The thickness of the diffusion layer is given by

$$\delta_m = 2r_p/\mathrm{Nu} \quad [16.7.131]$$

Then from Equations 16.7.106, 16.7.130 and 16.7.131

$$I = I_\infty [1 - \exp(-L/u\tau)] \quad [16.7.132]$$

with

$$I_\infty = \frac{\pi \epsilon \epsilon_o RTu}{2 n_t F} \mathrm{Nu} (1 - c_s/c_o) \quad [16.7.133]$$

From the correlation for the Nusselt number Nu

$$\mathrm{Nu} = 0.0223\, \mathrm{Re}^{7/8}\, \mathrm{Sc}^{1/4} \quad [16.7.134]$$

with

$$\mathrm{Re} = \frac{(2r_p)u}{\nu} \quad [16.7.135]$$

where ν is the kinematic viscosity (cm^2/s).

Then from Equations 16.7.133 and 16.7.134

$$I_\infty = \frac{0.035 \epsilon \epsilon_o RTu}{n_t F}\, \mathrm{Re}^{7/8}\, \mathrm{Sc}^{1/4} (1 - c_s/c_o) \quad [16.7.136]$$

Sc is the Schmidt number.

The concentration c_s should be sensitive to the surface materials, but since these are found to have only a small effect it is possible to assume $c_s \ll c_o$.

As described below, Equation 16.7.132 has had some success in describing the current generation in hydrocarbon liquids of low conductivity, but not for high conductivity hydrocarbon liquids. The treatment has therefore been extended by Koszman and Gavis utilizing the model of Klinkenberg and van der Minne. Starting with Equation 16.7.123, and introducing the Reynolds number

$$\mathrm{Re} = \frac{u d_p \rho_1}{\eta} \quad [16.7.137]$$

where η is the viscosity of the liquid (g/cm s) and ρ_l is the density of the liquid (g/cm^3), the friction factor f

$$f = \frac{\tau_{so}}{2\rho_1 u^2} \quad [16.7.138]$$

and the correlation for the friction factor

$$f = 0.079\, \mathrm{Re}^{-0.25} \quad [16.7.139]$$

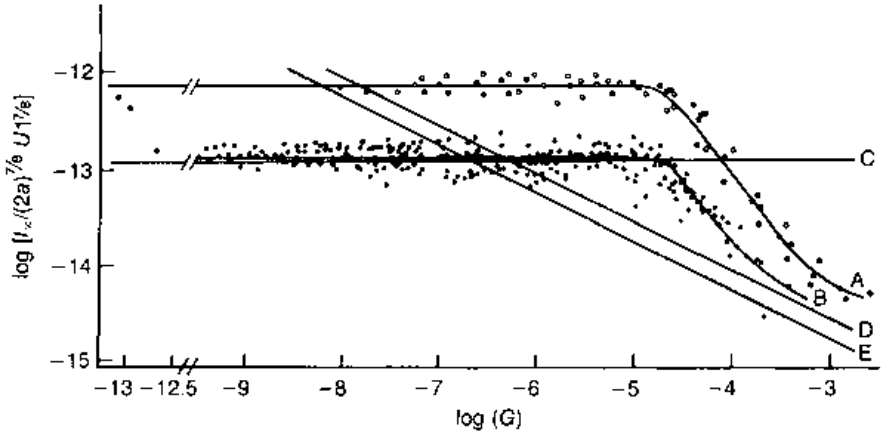


Figure 16.54 *Streaming current for liquid flow in a pipe (Koszman and Gavis, 1962b): A, B experimental curves for platinum, stainless steel tubes respectively. C, theoretical line for low conductivity liquids; D, theoretical line for high conductivity liquids, Re = 2100; and E, theoretical line for high conductivity liquids, Re = 45 000 (Courtesy of* Chemical Engineering Science*)*

yields

$$I = 0.04\pi\epsilon\epsilon_o \, \mathrm{Re}^{3/4} u\zeta \qquad [16.7.140]$$

The authors then write Equation 16.7.140 as

$$I = \frac{0.02\pi r_p \kappa\zeta}{G} \qquad [16.7.141]$$

with

$$G = \frac{4r_p^2}{\mathrm{Re}^{7/8}\tau\nu} \qquad [16.7.142]$$

From Equation 16.7.141 they derive

$$I = \frac{0.04 I_\infty \, \mathrm{Re}^{-1/8} \, \mathrm{Sc}^{-1/2}}{G^{1/2}} \qquad [16.7.143]$$

where I_∞ is given by Equation 16.7.133.

The high conductivity model of Equation 16.7.141 does not include a term which corrects for pipe length comparable to that in Equation 16.7.132, because the relaxation time is so short that the equilibrium current is reached in a very short distance.

The Koszman and Gavis model for low conductivity is Equations 16.7.132 and 16.7.133, and that for high conductivity is Equations 16.7.141 and 16.7.142.

Some features of the low conductivity model are:

$$I = f(\kappa) \qquad \text{Short pipes} \qquad [16.7.144a]$$

$$I_\infty \neq f(\kappa) \qquad \text{Long pipes} \qquad [16.7.144b]$$

$$I_\infty \propto u^{\frac{7}{8}} \qquad [16.7.145]$$

$$I_\infty \propto (2a)^{7/8} \qquad [16.7.146]$$

Koszman and Gavis performed experiments to study the charge generation in small diameter pipes. The experiments confirmed relations 16.7.144–16.7.146. They then plotted the group $(I_\infty/u^{\frac{7}{8}}(2a)^{7/8})$ against G, as shown in curve A of Figure 16.54. The graph shows that in the low conductivity region the group $(I_\infty/u^{\frac{7}{8}}(2a)^{7/8})$ is independent of G, as predicted by theory. This held for a wide range of liquid electrical conductivities, liquid velocities and a rather smaller range of pipe diameters and materials. The main exception was platinum pipes which gave a much higher current generation, as shown in curve B of Figure 16.54. The authors attributed this to a surface roughness effect.

The low conductivity model is not applicable, however, in the high conductivity region. Its range of applicability is for values of $\log_{10} G < -5$. For higher conductivities the current predicted is higher than that observed. At high conductivities the high conductivity model, Equation 16.7.141, was used. It gave the predicted values shown in curves C and D of Figure 16.54. The two curves are for the two extreme values of the Reynolds number used (2 100 and 45 000).

N. Gibson (1971) has cast the Koszman and Gavis model in the form

$$Y = Kf(G) \qquad [16.7.147]$$

with

$$Y = \frac{I_\infty}{u^{1.88} d^{0.88}} \qquad [16.7.148]$$

$$G = \frac{d^2}{\mathrm{Re}^{1.75}\tau\nu} \qquad [16.7.149]$$

$$K = \frac{0.35 RT\epsilon\epsilon_o}{n_t F \nu^{0.88}} \mathrm{Sc}^{0.25} f(C) \qquad [16.7.150]$$

where $f(C)$ is a concentration function.

Equation 16.7.147 applies to liquids of all conductivities. For the case of liquids of low conductivity in turbulent flow

$$f(G) = 1 \qquad [16.7.151]$$

The model of Equation 16.7.147 gives exponents for the pipe diameter d and the liquid velocity u which may be compared with values obtained in empirical correlations.

16.7.18 Schön model

Schön (1965) carried out experiments using pipe diameters in the range 2.5–20 cm and 'motor spirit' (resistivity 10^{-14}–$10^{-11}\,\Omega\,\mathrm{cm}$) and obtained the correlation

$$I_\infty = \beta(ur)^n \qquad [16.7.152]$$

where r is the pipe radius (cm), u is the liquid velocity (cm/s), β is a constant and n is an index. The value of n was in the range 1.8–2.0. The author states that the experimental scatter was such that a value of 2 may be taken for n. For this value of n the constant $\beta = 1.5 \times 10^{-13}$.

Equation 16.7.152 has been given by Klinkenberg (1967c) in SI units:

$$I_\infty = Cu^2d^2 \qquad [16.7.153]$$

where d is the pipe diameter (m), u is the liquid velocity (m/s) and C is a constant. The value of the constant C is given as $3.75 \times 10^{-6}\,\mathrm{A\,s^2/m^4}$.

Schön states that Equation 16.7.152 is intended to give an upper limit. It has been widely quoted in the literature and thus evidently is widely used.

A critique of Equation 16.7.152 has been given by Britton and Smith (1988), who indicate that it is not conservative in all cases and propose a revised value of C of $2.5 \times 10^{-5}\,\mathrm{A\,s^2/m^4}$.

16.7.19 Gibson and Lloyd model

Another set of experiments are those of N. Gibson and Lloyd (1967, 1970b), who utilized pipe diameters in the range 1.62–10.9 cm with toluene and toluene with ASA additive as a conductivity modifier.

They found that the Koszman and Gavis model broke down for these larger pipe diameters. They correlated their results using the equation

$$I_\infty = ku^{\mathrm{m}}d^{\mathrm{n}} \qquad [16.7.154]$$

where d is the diameter of the pipe (cm), u is the velocity of the fluid in the pipe (cm/s), k is a constant and m and n are indices. The indices m and n were somewhat variable, as was the constant, but N. Gibson (1971) has given Equation 16.7.154 as

$$I_\infty = ku^{2.4}d^{1.6} \qquad [16.7.155]$$

and the values of k given by N. Gibson and Lloyd (1970b) are then of the order of 10^{-14}.

The variability of the indices is taken into account in the alternative equation given by N. Gibson and Lloyd (1967) as follows:

$$I = 2.24 \times 10^{-11}d^{1.8}u^{1.45} + 0.01d\,\exp(0.4\,\log_{10}d\,\log_{10}u) \qquad [16.7.156]$$

where d is the pipe diameter (cm) and u is the liquid velocity (cm/s).* Equation 16.7.156 is another equation which is often quoted.

N. Gibson and Lloyd (1970a) also studied the effect of contamination on charge generation. They found that the presence of contaminant in the toluene could affect the charge generated, but that the values of the streaming current never exceeded those of pure toluene by a factor of more than 10. They attributed this effect to the influence of the contaminant on the electrical conductivity of the liquid.

*In the original paper, and in the first edition of this book, the index of d in Equation 16.7.156 was incorrectly preceded by a negative sign.

16.7.20 Other models

There are a number of other models for the charging current in liquid flow through pipes. They include those by Gibbings (1967) and Gibbings and Hignett (Gibbings and Hignett, 1966; Hignett and Gibbings 1968), Goodfellow and Graydon (1968a,b), Walmsley (1982, 1983a–c) and Walmsley and Woodford (1981a,b), and Abedian and Sonin (1982).

16.7.21 Liquid flow in non-conducting pipes

Most of the work done on streaming currents has been for metal pipes, but a small amount of work has been done on non-conducting, or insulating, pipes. In this context a non-conducting pipe is one made of a material such as glass, rubber or plastic. However, the point is often made that these materials can conduct the very low currents which occur in static electrification.

Work using 12 mm diameter polyethylene pipe with kerosene has been described by N. Gibson (1971). The main difference compared with results for metal pipes was that for a low conductivity liquid (resistivity 10^{10}–$10^{12}\,\Omega\,\mathrm{cm}$) the streaming current passed through a transient, decreasing with time to a constant value. For a high conductivity liquid the current was constant with time, as is the case for liquids of all conductivities in metal tubes. This decrease of current was attributed to the fact that the charge which separates to the pipe surface is unable to migrate along it sufficiently fast and impedes charge separation.

Work on the electrification of xylene in a glass pipe has been described by Cross, Haig and Cetronio (1977). These workers found a number of features which had a marked effect. There were high charge levels at bends and constrictions compared with straight pipe. Current flowing to metal flanges and to metal bands placed around the pipe varied both in magnitude and polarity. The state of the pipe surface was difficult to control and had a strong effect. For example, baking the pipe at 400°C effected a change in polarity.

16.7.22 Carruthers and Marsh model

Carruthers and Marsh (1962) have developed a model for the streaming current which is applicable to both conducting and insulating pipes. The model was developed as part of a study of the fuelling of aircraft where a filter in the pipe is liable to generate a large amount of charge. The model assumes that the liquid entering the system is already charged and deals with its subsequent behaviour. It does not itself provide an estimate of the streaming current in the liquid entering the pipe.

The simple model initially used was

$$I_{\mathrm{o}} = I_{\mathrm{i}}\,\exp(-t/\tau) + I_{\mathrm{p}}[1 - \exp(-t/\tau)] \qquad [16.7.157]$$

where I_{i} is the current entering the pipe (A), I_{p} is the current generated in the pipe (A), I_{o} is the current leaving the pipe (A) and t is the residence time in the pipe (s).

This model proved inadequate, however, and the following more complex model was developed. A conductance ratio B was defined as

$$B = \frac{\text{Conductance per unit length of liquid in pipe}}{\text{Conductance per unit length of liquid in pipe + pipe wall}} \quad [16.7.158]$$

so that

$$B = 0 \quad \text{Conducting pipe} \quad [16.7.159a]$$

$$B = 1 \quad \text{Insulating pipe} \quad [16.7.159b]$$

Then the general expression derived is

$$I = [I_i e^{-\lambda} + I_p(1 - e^{-\lambda}) + B(I_i - I_p)\left[\left(\frac{1 - e^{-\lambda}}{\lambda}\right) - e^{-\lambda}\right] \quad [16.7.160a]$$

with

$$\lambda = t/\tau \quad [16.7.160b]$$

For the two extreme cases

$$I_o = I_i f(\lambda) + I_p[1 - f(\lambda)] \quad [16.7.161]$$

with, for conducting pipe

$$f(\lambda) = e^{-\lambda} \qquad B = 0 \quad [16.7.162a]$$

and for insulating pipe

$$f(\lambda) = \frac{1 - e^{-\lambda}}{\lambda} \qquad B = 1 \quad [16.7.162b]$$

where f is the fraction of the charge unrelaxed.

The authors conducted experiments with 0.47 cm diameter pipe and *iso*-octane. Some of their results are shown in Figure 16.55. Figure 16.55(a) gives experimental data for copper pipe and Figure 16.55(b) data for PTFE pipe. They regarded these results as reasonable confirmation of the model.

Larger scale experiments using a $2\frac{1}{2}$ in. rubber hose were also performed and here the performance of the model using a rest conductivity was less good. However, the fit improved when an effective conductivity some 13 times lower than the rest value was used.

16.7.23 Liquid flow through filters and ball valves

Obstruction and filters in pipes can cause considerable increases in charge generation. Filters, in particular, can be prolific charge generators. For example, H. Kramer and Schön (1975) quote charge densities as high as 1000 C/m^3 obtained at filters. N. Gibson (1969) states that the current generated by a filter can be as high as 10^{-6}–10^{-5} A.

Factors which affect the charge generation at a filter include the porosity and pore diameter, the electrical conductivity of the liquid, and the superficial velocity of the liquid.

Experimental investigations of charge generation in filters include those of Gavis and Wagner (1967), Masuda and Schön (1967), Leonard and Carhart (1970) and Huber and Sonin (1975). The latter workers also give a model for the charge generation. The filters used by these various investigators were somewhat different and the original work should be consulted for the correlations obtained. The model of Carruthers and Marsh for the relaxation of charge after a charge generator such as a filter has already been described.

Work on charge generation in ball valves has been carried out by N. Gibson and Lloyd (1975). They performed experiments in a 10.9 cm stainless steel pipe with a 4 in. bore stainless steel ball valve with toluene and with toluene + water. Parameters investigated were the liquid velocity, the water content in the range 0–5% v/v and the fractional opening of the valve. Charge densities in the liquid increased with liquid velocity and with water content, the latter increase being marked for water contents above 0.1–0.2% v/v. Of the openings investigated, a fractional opening of 0.13 gave the highest charge generation. The highest charge density obtained in the work was 623 C/m^3 at a liquid velocity of 10 m/s with a water content of 5% v/v and a fractional opening of 0.13.

In addition to the effect such charging may have on a liquid flowing into a receiver, there is also a hazard of an incendive discharge at the valve itself. Gibson and Lloyd state that incidents have occurred where the valve body has been insulated by PTFE support rings and packing, and discharges have been observed during the flow of liquid. The capacitance of ball valves in the range 2–20 cm has been measured as 2–150 pF and the resistance to earth in the range 10^8–$10^{14}\,\Omega$. The authors take a potential of 1 kV as the minimum likely to give an incendive spark, and use a minimum ignition energy of 0.2 mJ. They are then able to compute the charging current required to give an incendive spark for different values of the valve capacitance, resistance to earth and potential using Equations 16.7.1, 16.7.6 and 16.7.19.

16.7.24 Liquid droplet settling

Klinkenberg and van der Minne (1958) have also given a treatment for liquid droplet settling, based on earlier work by von Smoluchowski (1921). For the settling of a drop of immiscible liquid, such as water, or of a solid particle, the downwards acting force in an electric field is

$$F_e = \tfrac{4}{3}\pi a^3 g\Delta\rho + qE \quad [16.7.163]$$

The upwards acting force is

$$F_e = 6\pi\eta a u \quad [16.7.164]$$

where a is the diameter of the liquid droplet (m), u is the settling velocity (m/s) and $\Delta\rho$ is the density difference between the droplet and the continuous liquid phase (kg/m^3).

Following Stokes' law, and equating these two forces

$$u = \frac{\tfrac{4}{3}\pi a^3 g\Delta\rho + qE}{6\pi\eta a} \quad [16.7.165]$$

The current caused by the transported charge is the sum of that from the falling droplets ($un_d q$) and that from conduction (κE). At equilibrium there is no net current and hence

$$un_d q + \kappa E = 0 \quad [16.7.166]$$

where n_d is the number of droplets per unit volume (droplets/m^3) and q is the charge on a droplet (C). But

$$n_d = \frac{X}{\tfrac{4}{3}\pi a^3} \quad [16.7.167]$$

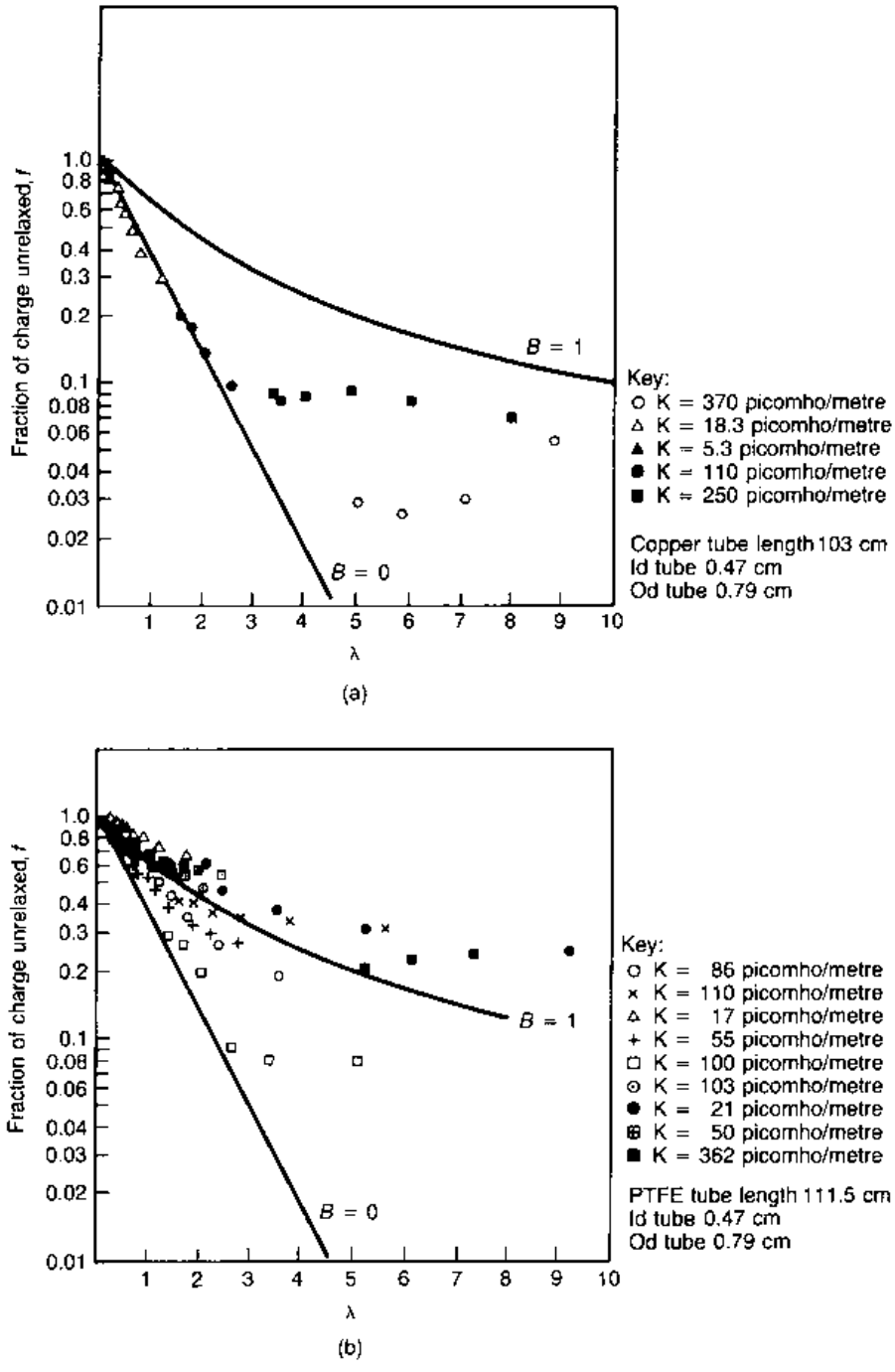


Figure 16.55 *Streaming current for liquid flow in a pipe (Carruthers and Marsh, 1962): non-conducting pipe: (a) charge relaxation in a copper pipe; and (b) in a PTFE pipe (Courtesy of the Institute of Petroleum)*

where X is the volume fraction of the dispersed phase (v/v).

From Equations 16.7.165–16.7.167

$$E = -\frac{qXg\Delta\rho}{6\pi\eta a\kappa\alpha} \quad [16.7.168]$$

with

$$\alpha = 1 + \frac{n_d q^2}{6\pi\eta a\kappa} \quad [16.7.169]$$

Also, the settling velocity is

$$u = \frac{2a^2 g\Delta\rho}{9\eta a} \quad [16.7.170]$$

$$= \frac{u_{st}}{\alpha} \quad [16.7.171]$$

where u_{st} is the Stokes velocity (m/s) and α is a correction factor.

Equation 16.7.168 contains the charge term q which is generally not known. It is more convenient to reformulate it in terms of the zeta potential, which can be estimated. From Equations 16.7.6 and 16.7.47

$$q = 4\pi\epsilon\epsilon_o a\zeta \quad [16.7.172]$$

Hence from Equations 16.7.168 and 16.7.172

$$E = -\frac{2}{3}\frac{\epsilon\epsilon_o}{\kappa}\frac{Xg\Delta\rho\zeta}{\alpha\eta} \quad [16.7.173]$$

with

$$\alpha = 1 + \frac{2X\kappa}{\eta}\left(\frac{\epsilon\epsilon_o\zeta}{\kappa a}\right)^2 \quad [16.7.174]$$

The settling potential gradient V_{set} is equal to the field strength E. The charge q_{ves} in the vessel is

$$q_{ves} = n_d q V_{ves} \quad [16.7.175]$$

where q_{ves} is the charge in the vessel (C), V_{set} is the settling potential gradient (V/m) and V_{ves} is the volume of the vessel (m^3).

The foregoing gives the field strength in the liquid. The field strength in the vapour space may be obtained by equating the potential differences so that

$$E_v = \frac{Eh_l}{H - h_l} \quad [16.7.176]$$

where E_v is the field strength in the vapour space (V/m), h_l is the height of liquid in the tank (m) and H is the height of the tank (m).

As an illustration, consider the estimate made by Howells (1993 LPB 114) for the settling of droplets of water from a foam blanket injected onto the top of a hydrocarbon fuel in a floating roof storage tank, as described in Section 16.28. He uses the following values of the parameters: $\epsilon = 2$, typical of hydrocarbons; $\epsilon_o = 8.85 \times 10^{-12}$ F/m; $\Delta\rho = 300$ kg/m^3, typical for the density difference between water and hydrocarbons; $\zeta = 0.04$ V, typically in the range 0.01–0.1 V; $\eta = 5 \times 10^{-4}$ Ns/m^2, typical of hydrocarbons; $\kappa = 0.1$ pS/m, typical of a very low conductivity product; $\alpha = 1$, constant dependent on particle size, which can be taken as unity for particles over a few hundred microns diameter; and $g = 9.81$ m/s^2. The value of X is obtained on the assumptions that a 0.3 m blanket of foam with an expansion ratio of 5 and a 25% drainage time is applied to the surface and that the foam breaks down into 750 μm droplets; this gives $X = 2.7 \times 10^{-4}$. Equation 16.7.173 then yields an electric field of 9 kV/m. Applied to a tank filled with liquid to a depth of 3 m earthed at the bottom, the liquid surface potential obtained is 27 kV.

16.7.25 Liquid sprays and mists

Another situation which can give rise to the generation of static charge is the break-up of a liquid to form a spray or mist. This can occur in two main ways: (1) discharge through an orifice, or (2) splashing against a surface.

The charge on a liquid droplet resides on the surface and exerts an outward force which is countered by surface tension. There is thus an upper limit to the amount of charge on a droplet, which was determined by Lord Rayleigh (1882), and is known as the Rayleigh limit. This may be written as

$$q = (64\pi^2\epsilon\epsilon_o\gamma a^3)^{\frac{1}{2}} \quad [16.7.177]$$

or

$$\left(\frac{q}{m}\right)_{max} = \left(\frac{36\epsilon\epsilon_o\gamma}{a^3\rho_l}\right)^{\frac{1}{2}} \quad [16.7.178]$$

with

$$m = \frac{4\pi a^3\rho_l}{3} \quad [16.7.179]$$

where a is the radius of the droplet (m), m is the mass of the droplet (kg), q is the charge (C), γ the surface tension of the liquid (N/m), ρ_l is the density of the liquid (kg/m^3) and the subscript max denotes the maximum. The Rayleigh limit is higher than the Gauss limit.

If a droplet is charged to the Rayleigh limit it disrupts. Work by Schweizer and Hanson (1971) on *n*-octanol showed that such a droplet then forms one particle with some 95% of the mass and some 77% of the charge, and a number of other, much smaller particles.

N. Gibson (1971) has reported work on the electrification of kerosene and of kerosene with 5% water released as a jet from a 3 mm pipe. Some results of this work are shown in Figure 16.56. The presence of relatively small amounts of water produced a 1000-fold increase in the space charge density.

Napier and Rossell (1973) studied the charge in a spray from a jet of xylene from a 0.25 mm tube. Space charge densities of 0.6×10^{-3} C/m^3 were measured. They comment that the conductivity of the liquid may have been increased by small amounts of water (up to 0.1%), oxidation products and dissolved metals.

After separation the liquid droplets retain their charge until they settle out or until a discharge occurs. A mist containing enough energy to give an incendive spark can be created by a high pressure jet, but the conditions under which discharge occurs are not well defined. Discharges observed have tended to be of the non-incendive corona type rather than spark discharges.

N. Gibson (1971) has given a simple model which treats the mist as a sphere containing uniformly sized droplets. The maximum field strength occurs at the periphery of the sphere and is

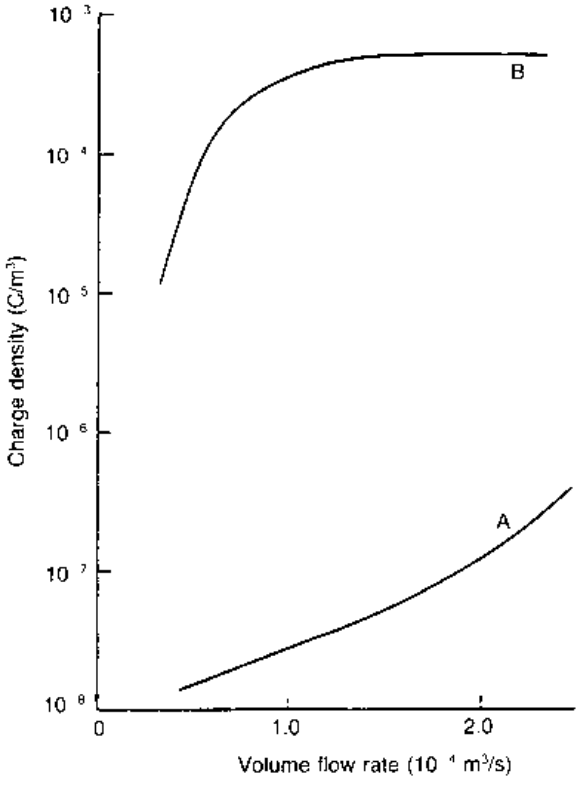


Figure 16.56 *Charge generated in a liquid jet (N. Gibson, 1971): A, kerosene; B, kerosene plus 5% water (Courtesy of the Institute of Physics)*

$$E_{max} = \frac{s a_{ms}}{3\epsilon_{ms}\epsilon_o} \qquad [16.7.180]$$

whilst the total energy of such a spherical mist cloud isolated in space is

$$W = \frac{2\pi s^2 a_{ms}^5}{9\epsilon_o}\left(\frac{1}{\epsilon_{ms}} + \frac{1}{\epsilon_{ar}}\right) \qquad [16.7.181]$$

where a_{ms} is the radius of the mist cloud (m), E is the field strength at the edge of the cloud (V/m), s is the space charge density of the mist (C/m^3), W is the energy in the cloud (J), ϵ_{ar} is the dielectric constant of air and ϵ_{ms} is the dielectric constant of the mist.

Another situation which can occur is where the jet impinges on a conducting object insulated from earth. A charge may accumulate on the object and then give a discharge.

These electrostatic effects occur when steam is let down from a high pressure so that it comes out wet from the orifice, as with a leak on a steam main. The principal hazard with such a leak is generally that presented by a conducting object insulated from earth.

An electrostatic charge can accumulate in droplets in steam. There is a static electricity hazard, therefore, when steam is used for cleaning or purging of equipment which has contained flammables.

Similarly, charge generation can occur when a vapour, such as propane, containing some small liquid droplets is let down through a jet.

Charge is also generated when a gas containing solid particles issues from an orifice. Thus a carbon dioxide jet being directed from a fire extinguisher into a vessel containing a flammable atmosphere may contain small particles of solid carbon dioxide and may generate enough charge to ignite the mixture.

The splashing of liquid falling onto, or directed against, a surface also results is charge generation. This has been studied by Iribane and Mason (1967), Jonas and Mason (1968), Levin and Hobbs (1971) and Vos (1971).

Levin and Hobbs showed that the main charging mechanism is disruption of the double layer at the liquid–air interface. Most of the charge is associated with the ejection of droplets of some 20 μm diameter from the liquid surface.

Vos obtained for aqueous solutions the following relation for the charging current

$$I = c^* u^2 \qquad [16.7.182]$$

where c^* is the charging tendency (A s^2/m^2), I is the charging current (A) and u is the velocity of the jet impinging on the surface (m/s).

16.7.26 Liquid agitation

The agitation of liquids can generate charges of the same order of magnitude as charging by liquid flow in a pipe. Vos *et al.* (1974) have described work undertaken following several fires involving agitation to effect the dissolution of epoxy resin in xylene. With epoxy resin flakes of 0.3–4 mm and with a liquid conductivity of 50 pS/m, the charge density increased from below 30 μC/m^3 at a stirrer speed of 250 rpm to 450 μC/m^3 at a speed of about 1250 rpm. Increasing the conductivity to 2000 pS/m led to a reduction in charge density to 10 μC/m^3. The charge density decreased with increase in temperature to an extent which could not be accounted for simply by the effect of temperature on conductivity.

Further studies of agitation charging have been described by H. Kramer (1981). Agitation may also be effected by blowing gas through the liquid. This also is liable to generate charge. Static electricity is also generated by splash filling of tanks.

16.7.27 Liquid storage tanks

Charge accumulation and relaxation are particularly important in relation to the filling of liquid storage tanks and of road and rail tankers. The storage tank problem has a number of different aspects: charge accumulation and relaxation; field strengths and potentials; and the generation of sparks, particularly incendive sparks. Some of the work in this field has been associated with the fuelling of aircraft.

16.7.28 Klinkenberg and van der Minne model

Klinkenberg and van der Minne (1958) have given a number of expressions for the electric field strength in

storage tanks. For a full spherical tank, Equation 16.7.57 is applicable and they also suggest its use for tanks that are cubic in shape. For long shallow tanks they refer to Equation 16.7.56.

For a partially full tank with a uniform charge density in the liquid but otherwise no liquid surface charge and zero charge density in the vapour space, they give the following relation for the field strength in the vapour space

$$E_v = \frac{s h_l^2}{2\epsilon_o(\epsilon_v h_l + \epsilon_l h_v)} \qquad [16.7.183]$$

where E_v is the field strength in the vapour space (V/m), h_l is the depth of liquid (m), h_v is the height of the vapour space (m), ϵ_l is the dielectric constant of the liquid and ϵ_v is the dielectric constant of the vapour.

16.7.29 Vellenga model

Vellenga (1961) obtained a model for the electric field strength inside a rectangular tank. He assumes that the charge is uniformly distributed and that the dielectric constant of the liquid and of the vapour are the same, the difference between them being in practice a factor of about 2. He obtained for the general case the expression

$$E_\gamma = \frac{1}{2}\frac{sc}{\epsilon\epsilon_o}\left[w^2 - \sum_{n=1}^{n=\infty} A_n(\cos \pi n w - 1)\cos \pi n \gamma\right] \qquad \gamma > w \qquad [16.7.184]$$

with

$$A_n = \frac{4}{\pi^2}\frac{1}{n^2 \cosh(n\pi/2\beta)} + \frac{16}{\pi^3}\sum_{m=1}^{m=\infty} \sin(m\pi/2)/[mp^2 \cosh(p\pi/2\alpha)] \qquad [16.7.185]$$

$$\alpha = c/a \qquad [16.7.186]$$

$$\beta = c/b \qquad [16.7.187]$$

where a, b and c are the length, width and height of the tank (m), respectively, E_γ is the field strength at the fraction of the tank height γ (V/m), w is the fraction of the height filled with liquid, α and β are shape parameters, and γ is the fraction of the tank height at which the field strength is measured.

For the particular case of a tank whose height is small relative to its lateral dimensions, Vellenga obtains

$$E = \frac{1}{2}\frac{scw^2}{\epsilon\epsilon_o} \qquad [16.7.188]$$

16.7.30 Carruthers and Wigley model

Carruthers and Wigley (1962) developed a model for the field strength and potential in a partially filled rectangular metal storage tank filled with uniformly charged liquid. They then extended this model to give the fields produced by a charge on the surface of the liquid and in the mist in the vapour space above it.

The space charge density s is given by

$$s = \frac{I_o \tau}{V_{ves} t} \qquad t \gg \tau \qquad [16.7.189]$$

where I_o is the current entering the tank (A), t is the time of filling (s) and V_{ves} is the volume of the liquid in the tank (m^3).

For a point in the vapour space with the co-ordinate x, y, z as measured from the top of the tank, the approximate field strength in the z direction E_z is

$$E_z = \frac{16s}{\epsilon_o \pi^3 (1/a^2 + 1/b^2)^{\frac{1}{2}}} \times \frac{(\cosh\beta d - 1)\cosh\beta z \sin(\pi x/a)\sin(\pi y/b)}{\epsilon_v \cosh\beta p \sinh\beta d + \sinh\beta p \cosh\beta d} \qquad [16.7.190]$$

with

$$\beta = \pi^2\left(\frac{1}{a^2} + \frac{1}{b^2}\right) \qquad [16.7.191]$$

where a is the length of the tank (m), b is the width of the tank (m), d is the height of the liquid (m), p is the height of the vapour space (m), ϵ_l is the dielectric constant of the liquid and ϵ_v is the dielectric constant of the vapour.

The authors also derive the space charge densities and field strengths for any mist existing in the vapour space in the tank. They consider two cases: (1) a tank filled with mist and (2) a tank half filled with liquid and half with mist. In this treatment they assume a cubical tank of length a. For the first case the field strength is at a maximum at the centre of each wall and is

$$E_{mf} = \frac{64}{3}\frac{a s_{mf}}{\epsilon\epsilon_o \pi^4} \qquad [16.7.192a]$$

$$E_{mf} = 6.79\frac{a s_{mf}}{\epsilon\epsilon_o \pi^3} \qquad [16.7.192b]$$

where E_{mf} is the maximum field strength with the tank full of mist and s_{mf} is the space charge density with the tank full of mist. For the second case, from Equation 16.7.190 and setting $d = p = a/2$, the maximum field strength in the vapour space is

$$E_{mh} = 2.84\frac{a s_{mh}}{\epsilon\epsilon_o \pi^3} \qquad [16.7.193]$$

where E_{mh} is the maximum field strength in the vapour space with the tank half full of liquid (V/m) and s_{mh} is the space charge density with the tank half full of liquid (C/m^3).

It can then be shown that in some circumstances a charged mist may produce a field strength of the same order as that of a charged liquid. Thus, assuming that in the first case all the liquid entering the tank in a time equal to the relaxation time τ forms a mist, the space charge density is

$$s_{mf} = \frac{I_o \tau}{a^3} \qquad [16.7.194]$$

whilst in the second case the space charge density is

$$s_{mh} = \frac{2 I_o \tau}{a^3} \qquad [16.7.195]$$

From Equations 16.7.192 and 16.7.194 for the first case and equations 16.7.193 and 16.7.195 for the second, the maximum field strengths are, respectively,

$$E_{mf} = 6.79\frac{I_o\tau}{\epsilon\epsilon_o\pi^3 a^2} \qquad t = \tau \qquad [16.7.196]$$

and

$$E_{mh} = 5.68\frac{I_o\tau}{\epsilon\epsilon_o\pi^3 a^2} \qquad t \gg \tau \qquad [16.7.197]$$

16.7.31 Vellenga and Klinkenberg model

As already mentioned, there is frequently an appreciable difference between the effective and rest conductivities of the liquid. One consequence of this is that during the relaxation of charge in a liquid following the filling of a tank, the relaxation time constant, given by Equation 16.7.27, is not in fact constant and the decay of the charge does not then follow the exponential decay given by Equation 16.7.78.

Vellenga and Klinkenberg (1965) have derived an alternative expression for charge decay based on the assumption that the conductivity of the liquid is proportional to the charge density. Considering a small element of volume V with space charge density s and hence a charge Vs, application of Gauss law, Equation 16.7.34, gives

$$\int D_n \, dA = sV \qquad [16.7.198]$$

where D_n is the component of D normal to an element of surface dA. The rate of loss of charge from dA is the current density J_n and that from the whole element is the current density J. Then from Equations 16.7.26, 16.7.27, 16.7.97 and 16.7.198

$$\frac{1}{\tau}\int D_n \, dA = -\frac{d(sV)}{dt} \qquad [16.7.199]$$

Integrating Equation 16.7.199 gives

$$\frac{ds}{dt} = -\frac{s}{\tau} \qquad [16.7.200]$$

Taking the limiting case where all the ions of one sign are removed, as described in Section 16.7.12, and substituting from Equations 16.7.107 and 16.7.108 in Equation 16.7.200

$$\frac{ds}{dt} = -\frac{us^2}{\epsilon_o\epsilon} \qquad [16.7.201]$$

Integrating Equation 16.7.201 yields

$$s = \frac{s_o}{1 + t/\tau_o} \qquad [16.7.202]$$

where s_o is the initial charge density and τ_o is the initial relaxation time.

Equation 16.7.202 is a hyperbolic equation and the authors describe it as the hyperbolic law of relaxation. Another hyperbolic decay model is that of M.D. Foster (1967). A number of workers have reported decay of charge in tanks which approximates more closely to the hyperbolic than to the exponential law.

16.7.32. Kramer and Schön model

H. Kramer and Schön (1975) have carried out a series of fundamental studies of the static electricity hazard in storage tanks, including the charging current entering the tank, the distribution of charge in the liquid, the field strength in the liquid and in the vapour space and the effect of bodies which distort this field, the incendivity of sparks produced and development of rules for tank filling.

With regard to the charge distribution, the authors postulate that the charge is not uniformly distributed within the liquid but is concentrated in a charge cloud. They estimate the volume of this charge cloud as

$$V_e = Q\tau \qquad [16.7.203]$$

where Q is the volumetric flow of liquid (m^3/s) and V_e is the volume of the charge cloud (m^3), this volume being that at the surface of which the charge density has decayed to $1/e$ of its original value. This model is based on laminar flow. For turbulent flow the cloud would be somewhat larger.

Kramer and Schön made measurements in a $15\,m^3$ tank, near the fill pipe outlet and at the far end of the tank, of the relative field strength, or field strength divided by total charge in the tank, at different filling rates, and plotted the relative field strengths at these two points vs the volume of the charge cloud. Whereas the relative field strength at the fill pipe was virtually constant, that at the far side of the tank was constant at high charge cloud volumes but fell off rapidly for charge cloud volumes below $2\,m^3$. The authors suggest that these results indicate that the effective charge cloud volume was some five times the nominal value given by Equation 16.7.203.

A further detailed study of the space charge cloud is given by Schön and Masuda (1969) and Schön and Kramer (1971).

H. Kramer and Schön (1975) then discuss the problem of field strength. They comment that the model of Carruthers and Wigley may not be applicable to large tanks containing high conductivity liquids. In any event, features such as the fill pipe distort the field, and this is crucial.

They treat the fill pipe as a cylindrical object. For such a configuration the relation between the potential and the field strength is

$$\phi_{max} = Er_1 \ln(r_2/r_1) \qquad [16.7.204]$$

where r_1 and r_2 are the radii of the inner and outer cylinders (m) and ϕ_{max} is the maximum potential in the centre of the tank in the absence of the fill pipe (V). The inner cylinder is the radius of the fill pipe and the outer one may be equated with a suitable lateral dimension of the tank.

They measured the field strength at the fill pipe in a large tank and a tank truck as

$$E = 7.5 \times 19^9 q \qquad \text{Large tank} \qquad [16.7.205a]$$

$$E = 30 \times 10^9 q \qquad \text{Tank truck compartment} \qquad [16.7.205b]$$

where q is the charge (C).

Then from Equation 16.7.204 they obtained the maximum potential ϕ_{max} as

$$\phi_{max} = 1.9 \times 10^9 q \qquad \text{Large tank} \qquad [16.7.206a]$$

$$\phi_{max} = 5.0 \times 10^9 q \qquad \text{Tank truck compartment} \qquad [16.7.206b]$$

The smaller tank therefore had the higher maximum potential. The authors state that the Carruthers and Wigley model gives the maximum potential as inversely proportional to the diagonal of the mid-height cross-sectional area, and that their results confirm this.

They then consider the incendivity of discharges. For an incendive discharge there is a critical radius of curvature below which an incendive spark is unlikely. This radius is about 5 mm. For small radii of curvature above this value

$$E_e r = 35\,000 \qquad 5 \times 10^{-3} \leq r \leq 12 \times 10^{-3} \qquad [16.7.207]$$

where E_e is the field strength for the onset of incendive discharge (V/m) and r is the radius of curvature (m). For larger radii

$$E = 3\,000\,000 \qquad r > 12 \times 10^{-3} \qquad [16.7.208]$$

With a small probe the potential distribution in the vicinity of the probe is changed only locally. The undisturbed potential ϕ at the probe determines the field strength E at the surface of the probe according to the relation

$$Er \approx \phi \qquad [16.7.209]$$

Then from Equations 16.7.207–16.7.209 an incendive spark is unlikely as long as the maximum potential in the vapour space is kept below 35 kV.

Kramer and Schön consider two limiting cases: (1) a tank with a probe and (2) a tank with a fill pipe only. These two cases correspond, therefore, to field strengths for the onset of an incendive discharge of 35 kV and 3000 kV, respectively.

For the first case, from relations 16.7.207–16.7.209 and taking account of the empirical factor of 0.6 for the maximum potential

$$0.6\phi_{max} \leq 35\,000 \qquad [16.7.210]$$

The streaming current entering the tank and the total charge in the tank are

$$I_o = \frac{\pi d^2 u s_o \epsilon \epsilon_o}{4\kappa_e} \qquad [16.7.211]$$

$$q = I_o \epsilon \epsilon_o / \kappa_e \qquad [16.7.212]$$

where d is the diameter of the fill pipe (m), I_o is the charging current in the liquid entering the tank (A), s_o is the charge density of that liquid (C/m^3), u is the liquid velocity (m/s) and κ_e is the effective conductivity of the liquid (S/m).

Then from Equations 16.7.206 and 16.7.210–16.7.212

$$\frac{s_o u d^2}{\kappa_e} \leq 2.2 \times 10^6 \qquad \text{Large tank} \qquad [16.7.213a]$$

and

$$\frac{s_o u d^2}{\kappa_e} \leq 0.83 \times 10^6 \qquad \text{Tank truck compartment} \qquad [16.7.213b]$$

For the second case

$$E_e \approx 3\,000\,000 \qquad [16.7.214]$$

and assuming that the field strength at the fill pipe is

$$E \propto 1/d \qquad [16.7.215]$$

Equations 16.7.205, 16.7.211, 16.7.212 and 16.7.214 yield

$$\frac{s_o u d}{\kappa_e} \leq 1.2 \times 10^8 \qquad \text{Large tank} \qquad [16.7.216a]$$

$$\frac{s_o u d}{\kappa_e} \leq 0.6 \times 10^8 \qquad \text{Tank truck compartment} \qquad [16.7.216b]$$

The relationship between the effective conductivity and the rest conductivity proposed by the authors in this context is

$$\kappa_e = \kappa_r / 2 \qquad [16.7.217]$$

From these relations the authors give the limiting filling criteria shown in the table at the bottom of the page.

Where, for a container of lateral dimensions a and b, L is the length of the diagonal, calculated from $L = (a^2 + b^2)^{\frac{1}{2}}$.

The relation for other tank sizes utilizes scaling based on the diagonal of the mid-height-cross-sectional area. These are limiting criteria which do not include a safety factor. The authors also quote the following German safety rule:

$$u^2 d \leq 0.64 \qquad [16.7.218]$$

For liquids with very low conductivities the treatment described may be too restrictive. The streaming current is likely to be lower and may not reach its steady-state value. The authors state that experimental evidence suggests that a limiting rest conductivity of 0.8 pS/m may be applied.

This treatment is applicable only to conditions where there are no generators of unusually large amounts of charge, such as a liquid velocity above 7 m/s, water in the liquid or a filter in the inlet pipe. Also the treatment applies to tank sizes up to those of a tank car. For larger tanks the assumption of a uniform charge density breaks down, because the effective relaxation volume is small compared with the tank volume.

Filling condition			*Projections permitted*
Tank truck	*Rail tank car*	*Other tanks*[a]	
$u^2 d \leq 6.2 \times 10^{12} \kappa_r$	$u^2 d \leq 12.4 \times 10^{12} \kappa_r$		Fill pipe only; outlet fully covered by liquid
$ud \leq 0.29 \times 10^6 \kappa_r$	$ud \leq 0.47 \times 10^6 \kappa_r$	$ud \leq 0.17 \kappa_r^{\frac{1}{2}} L^{\frac{1}{2}}$	Projections of all kinds permitted

[a] Where, for a container of lateral dimensions a and b, L is the length of the diagonal, calculated from $L = (a^2 + b^2)^{\frac{1}{2}}$.

16.7.33 Road and rail tankers

As described in Section 16.7.2, a large proportion of the incidents attributed to ignition by static electricity have involved road tankers and rail tank cars. The work of H. Kramer and Schön (1975) on tanks in general and road and rail tankers in particular was described in Section 16.7.32.

An early study of the static ignition hazard in filling road tankers was made by Herzog, Ballard and Hartung (1961). They considered three paths for a discharge: (1) between two points on the liquid surface, (2) between the liquid surface and the tank wall and (3) between the liquid surface and a probe. They concluded that the latter was the principal hazard.

These authors developed the concept that the approach of an earthed probe can cause a very high charge to build up on the liquid surface. A system composed of a liquid surface and a probe is a capacitor. Capacitance is inversely proportional to separation. Therefore as the probe approaches the liquid surface, or rather as the liquid surface during filling approaches the probe, with the charge initially being constant, the liquid surface potential at the point near the probe will drop according to Equation 16.7.6. The difference in liquid surface potentials thus created will cause the charge to move in order to equalize the potentials. They carried out experimental work and found that at lower flow rates there was little difference in potential between a point near the probe and one some distance away, so that there was a degree of charge concentration, but that at higher flow rates a potential difference developed and the charge concentration was less; they attributed this latter condition to the increased turbulence.

They found that the design of the fill pipe had a marked effect on its capacitance. The pipe capacitance decreased linearly with the separation between the pipe and the liquid surface up to a separation of 0.1 in. The lowest separation at which capacitances were measured was 0.02 in but capacitance values were extrapolated back to a separation of 0.0025 in. The pipe design with the lowest capacitance at 0.0025 in. was one with a 45° slant end, with a capacitance of 140 pF. Other designs were, in ascending order of capacitance, an open pipe end, a T deflector and a cone deflector, the latter having the highest capacitance at 470 pF. The liquid surface potentials measured in this work were up to 10 kV.

Mahley and Warren (1968) carried out an investigation in which the effect of the following parameters was studied: (1) fill tube design, (2) liquid velocity, (3) compartment height, (4) fill tube height, (5) liquid conductivity, (6) liquid wetness, (7) air bleed and (8) filter.

They found that the design of the fill tube had a marked effect on the potential of the liquid surface. The lowest potential was obtained with the 45° slant end pipe. The ranking of the other devices was generally, in ascending order of potential, an open pipe end, a T deflector and a cone deflector.

Drop heights of < 2, 30 and 60 in. were used. The difference in liquid surface potential between the first two drop heights was minimal, but use of a 60 in. drop height gave much higher potentials.

The liquid surface potential increased with liquid velocity, with water content and with the use of a filter. The increase in potential with liquid velocity was more than proportional and the magnitudes were much higher for fill tube designs other than the slant end one. The increase in potential when a filter was used was large.

The effect of liquid conductivity was somewhat complex. The conductivity range studied was 2.5–100 cu (pS/m). In this range, use of a conductivity additive caused the liquid surface potential to decrease with the resultant increases in liquid conductivity. But the results for undoped liquid did not show this regular variation. A liquid with 16 cu gave a higher potential than one with 2.5 cu.

The effect of an air bleed, which might occur due to equipment malfunction upstream, was simulated using a nitrogen bleed, but this appeared to have a minimal effect on the liquid surface potential.

The account of this work just given is necessarily simplified. There was considerable interaction between the different variables, with mutually enhancing or reducing effects.

The liquid surface potentials measured in this work were up to almost 50 kV, the latter value being obtained with a liquid conductivity of 16 cu, a liquid velocity of 30 ft/s, a fill tube with cone deflector and a drop height of 60 in.

Tank truck loading has been studied by Ginsburgh and o-workers (L. Wright and Ginsburgh, 1963; Bulkley and Ginsburgh, 1968) with special reference to charge relaxation and discharge incendivity.

L. Wright and Ginsburgh (1963) investigated discharges. They present a model which shows that the controlling features of the discharge are the potential of the liquid surface and the geometry of the probe. They report experiments on discharges induced by applying power between a liquid surface and a probe, including a 3 in. diameter vertical pipe, a vertical plate and a horizontal plate. For the pipe the potentials for onset of a discharge were 25 kV at a separation of $\frac{1}{2}$ in. and 50 kV at one of 1 in. When power was applied the liquid rose towards the probe, and for separations of less than $\frac{1}{2}$ in. it touched the probe.

Bulkley and Ginsburgh (1968) continued this work on discharges. The minimum ignition energy normally quoted, say > 0.25 mJ for hydrocarbons, applies only to a spark gap of optimal shape and separation and to a near-stoichiometric mixture. They suggest that, in practice, the energy required to give an incendive spark is at least an order of magnitude greater.

The spark between a liquid surface and a probe is quite different from that between two metal electrodes. Although concentrated at the probe, it branches over a relatively large part of the liquid surface.

The authors state that most of the sparks obtained in the work of Wright and Ginsburgh did not possess enough energy to be incendive. For an incendive spark to occur the liquid surface potential must exceed 20 kV which requires a charge density of $30\,\mu C/m^3$. They propose that a charge density of $15\,\mu C/m^3$, incorporating a safety factor of 2, be taken as the safety limit.

Bulkley and Ginsburgh point out that over the years oil products have become much purer so that their conductivity is much less, with corresponding increases in relaxation times from seconds to minutes. One consequence of this is that the residence time of typically 30 seconds in tanks, provided to allow relaxation, is no longer adequate.

16.7.34 Strawson and Lyle model

Strawson and Lyle (Lyle and Strawson, 1971, 1972, 1973; Strawson and Lyle 1975a,b) have reported an extensive programme of work by Shell on the safe loading of road and rail tankers.

Lyle and Strawson (1971) conducted experiments in which they studied discharges between a charged liquid surface and a fill pipe when a tank is filled with charged fuel. The fuel was gas oil with a conductivity of 2–7 pS/m. The locus of the liquid inlet charge density limit curve for onset of discharge ranged from an inlet liquid charge density of about $200\,\mu C/m^3$ at low liquid inlet velocities down to less than $20\,\mu C/m^3$ at high velocities. The discharge energies were determined to be about 0.005 mJ.

A separate experiment was conducted to determine the energy in an incendive discharge between a liquid surface and a probe. The liquid used was kerosene with a propane–air mixture in the vapour space around the probe. Liquid entering the tank was given a high charge by passing it through a filter. The energy required to achieve ignition was 4.7 mJ. This compares with the normal minimum ignition energy of 0.2 mJ.

In an extension of this work, Strawson and Lyle (1975b) performed experiments in three metal tanks of 1.2, 2.3 and $5\,m^3$ volume and with overhead and bottom filling pipes. They investigated the conditions for discharge between the liquid surface and the fill pipe or a gauge marker. They developed a model for the discharge conditions. In addition to determining the locus of the liquid inlet charge density limit curve for the onset of discharge as a function of liquid inlet velocity for a fixed tank length, they also obtained both experimentally and theoretically the locus of that curve as a function of tank length for a fixed liquid inlet velocity. The locus passed through a minimum for a tank length of about 2 m. For this tank length the authors determined the limiting liquid inlet charge density as $20\,\mu C/m^3$.

The authors state that no sparks were obtained with liquids with conductivities greater than 4 pS/m.

Strawson and Lyle went on to consider the parameters which might be taken as the basis of safety, the field strength and the potential. In particular they discuss the criterion of field strength at the filling tube used by Kramer and Schön (Schön and Kramer, 1971; H. Kramer and Schön, 1975). This model is based on a charge distribution in the liquid around the fill pipe. They argue that the charge distribution is more likely to be relatively uniform. At the high filling rates, which are of prime interest, turbulence will tend to equalize the charge density. Moreover, Kramer and Schön have shown that for a low conductivity liquid the charge density is uniform even in large tanks.

The alternative is to use the potential of the liquid surface. Strawson and Lyle conclude that this is the better criterion. They assume that the charge is uniformly distributed and define the relevant potential as that existing in the absence of any protrusion. Various limiting values of this potential have been proposed. Mahley and Warren (1968) have proposed 1 kV, based apparently on the work of Herzog, Ballard and Hartung (1961), but the authors regard this as too low. They refer to the value given by Kramer and Schön of 35 kV. They state that in their own work the minimum potential for incendive discharge was 45 kV, and propose this as the limit value.

A model was developed for the potential of the liquid surface which gives

$$\phi \propto s_t\, f(\text{tank dimension, liquid depth}) \qquad [16.7.219]$$

where s_t is the space charge density in the liquid in the tank (C/m^3) and ϕ is the potential of the liquid surface (V). The charge density in the tank is in turn related to that in the liquid entering the tank according to the relation

$$s_t = \frac{s_o Q \tau}{V_{ves}}[1 - \exp(-t/\tau)] \qquad [16.7.220]$$

where Q is the volumetric flow of the liquid entering the tank (m^3/s), s_o is the space charge density of the liquid entering the tank (C/m^3), and V_{ves} is the volume of liquid in the tank (m^3).

From Equations 16.7.219 and 16.7.220, the authors derive their guideline for safe filling conditions:

$$ud \leq \left[\frac{k\kappa u}{s_o} f(L)\right]^{\frac{1}{2}} \qquad [16.7.221]$$

where d is the fill pipe diameter (m), L is the length of the tank (m), s_o is the inlet charge density ($\mu C/m^3$), u is the liquid inlet velocity (m/s), κ is the liquid conductivity (pS/m) and k is a constant.

In subsequent work, Strawson and Lyle (1975a) obtained limiting values of the group $s_o/\kappa u$. Their results are shown in Figure 16.57, which gives the following limits:

$s_o/\kappa u$ $(\mu C/s(pS\ m^3)^{-1})$	
≤ 1.8	Tests at filling stations
≤ 3.3	Experiments
≤ 12.5	Experiments with partially blocked filter

Also shown in Figure 16.57 are the limit lines given by the model of Schön (1962a) for charge generation in a pipe, which are a function of the residence time in the pipe, and hence of the pipe length. From this work Strawson and Lyle propose a limiting value for the group $s_o/\kappa u$ of 12.5.

Using this limit value in Equation 16.7.221 together with appropriate values of $kf(L)$, the authors obtain the following guidelines for safe filling:

Filling mode	*Tank length*			
	≤ 2 m		>2 m	
	kf(L)	ud	kf(L)	ud
Top filling	3.1	≤ 0.50	3.1 $(L/2)^{\frac{1}{2}}$	0.50 $(L/2)^{\frac{1}{2}}$
Bottom filling	1.6	≤ 0.36	1.6 $(L/2)^{\frac{1}{2}}$	0.36 $(L/2)^{\frac{1}{2}}$

The criteria for bottom filling allow for a central protrusion from the roof. In addition, a further overall limit is imposed to limit the field created by the jet:

$$ud \leq 0.77 \qquad [16.7.222]$$

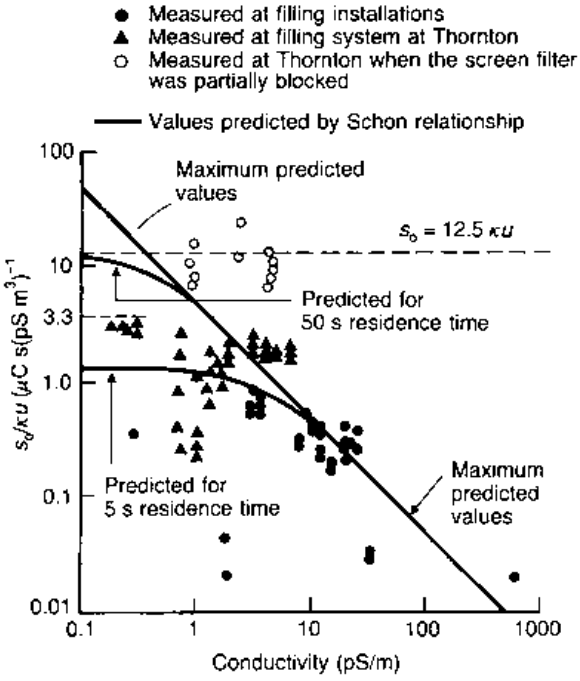


Figure 16.57 *Charge generated at filling stations (Strawson and Lyle, 1975a) (Courtesy of the Institution of Electrical Engineers)*

This treatment contains a number of assumptions which are therefore the conditions for its applicability. Three of these are: that the charge distribution in the liquid is uniform; that the charge generation due to splashing can be neglected; and that any charge density transient at start-up can be neglected. The authors regard these criteria as being confirmed experimentally. With regard to the conductivity of the liquid, it is assumed that the ratio of the effective to the rest conductivity is the same as in the experiments and that the inlet liquid charge density is proportional to the liquid conductivity. Further restrictions are the absence of high charge generation conditions, specifically water in the liquid or a filter in the pipe, and absence of insulated conductors in the system or tank.

16.7.35 Kramer and Schön model

The work of Kramer and Schön on the filling of tanks in general and of road and rail tankers in particular, was described in Section 16.7.32. This work provides another set of guidelines for tanker filling.

16.7.36 Rees model

Another extensive programme of work on the safe loading of road and rail tankers is that carried out by BP, as described by W.D. Rees (1981). Rees describes experimental work on discharges between a charged liquid surface and a metal probe. In this work it proved relatively easy to obtain discharges which would ignite a propane–air mixture with negatively charged liquids at liquid surface potentials as low as 25 kV, but ignition did not occur with positively charged liquids even at potentials as high as 80 kV. It was found that a charge transfer in the discharge of at least 75 nC was required for ignition. The shape and dimensions of the probe affected ignition. The shape most favourable to ignition was a sphere, then a hemisphere and then a rod. Using a 28 mm sphere with the most ignitable propane–air mixture the probability of ignition was close to unity, provided the charge transfer exceeded 75 nC.

Rees summarizes the principal guidelines for safe filling as follows. The criterion of the Physikalische Technische Bundesanstalt (PTB) is

$$ud \leq 0.38 \qquad [16.7.223]$$

The Shell criteria are

$$ud \leq 0.50 \qquad [16.7.224]$$

and

$$s_o/\kappa u \leq 12.5(\mu\text{C s(pS m}^3)^{-1}) \qquad [16.7.225]$$

The criterion given by Equation 16.7.224 is criticized insofar as the work described on incendive discharges has shown that critical values of the group $s_o/\kappa u$ can be less than 12.5. The critical values depend on the pipe diameter, the liquid conductivity and the liquid inlet velocity; values down to 2.4 are quoted.

Rees refers to four incidents which have occurred in Canada with a loading limit $ud \leq 0.5$, and two in Germany with a loading limit $ud \leq 0.37$.

Rees states the BP view that it is not possible to determine a loading velocity which is completely safe, but that it can be said that reducing the velocity reduces the risk. The PTB guideline is preferred and, in order to avoid proliferation of guidelines, is the one adopted.

However, he also puts forward for discussion the following proposals for loading limits:

Liquid conductivity (pS/m)	*Loading rate, ud*
$\kappa \geq 10$	≤ 3500 l/min
$5 \leq \kappa \leq 10$	≤ 0.5
$\kappa < 5$	≤ 0.38

16.7.37 Oil and chemical tankers

As described in Section 16.7.2, some of the most serious incidents attributed to ignition by static electricity have involved oil tankers. An early study of the problem is that of Bustin (1963). Following the *Esso Paterson* explosion in 1956 the company adopted a set of safety rules to reduce the static ignition hazard. The investigation described was to assess the effectiveness of these safety rules.

Bustin considers the following conditions: (1) loading of product, (2) steam cleaning, (3) water washing, and (4) ventilation.

He describes an extensive series of tests on the loading of tankers. Charge densities of up to 0.2 μC/m^3, liquid surface potentials of 10 kV and field strengths of 4 kV/m were calculated from these tests. The author states that whilst at these potentials discharge would not occur to normal tank internals, it might well to a pointed

probe. He therefore lays emphasis on ensuring that there are no earthed probes or insulated conductors.

The cleaning of tanks using steam has been associated with a number of explosions. Tests by BP some years previously showed that if the steam cleaning machine was not earthed, or lost its earth connection, a high potential could build up on it and, in the event of a discharge, the spark was likely to incendive. Isolated conductors in particular are a hazard in this respect. With regard to the steam cloud itself, faint discharges were detected. The highest field strength determined was 60 000 V/m, which indicates that a volume of steam equivalent to a sphere some 1.25 m diameter would need to discharge to give an incendiary spark. The author states that steam cleaning is to be avoided; in fact it is frequently banned. The main method of cleaning tanks is water washing. This the author regards this as safe.

Rapid ventilation may be used for gas freeing. But there was concern that charge generation could occur due to the presence of rust particles or fuel droplets in the air. Tests were performed in which the conditions in a ventilation pipe were measured. At 510 cfm of air, an air velocity of 170 ft/s and a dust loading of 0.016 lb/ft^3 the charging current was 5×10^{-6} A and the calculated field strength at the pipe wall was 50 kV/m. This was considered close to the region where discharges might occur, though not necessarily incendive ones. In fact even abnormally high dust loadings did not lead to ignition unless an insulated conductor was present.

Bustin states that neither water washing nor ventilation necessarily ensure the elimination of a flammable mixture.

Following the three tanker explosions in 1969, a major programme of work was undertaken by Shell. Some of the results were described in a set of papers by van der Meer (1971), van der Weerd (1971), Smit (1971) and Vos (1971).

The work described by van de Weerd (1971) was concerned with water washing. A typical washing machine operates at 10 bar giving 180 m^3/h of water with a jet velocity of 40 m/s. The jet diameter is 4 cm at the nozzle increasing to 1–3 m at the wall. Quite large amounts of air are entrained. The mist formed has a density of about 1 g/m^3. Mist formed by impact at the wall is charged.

The factors studied were (1) number and type of washing devices, (2) jet velocity, (3) water temperature, (4) type of water, (5) impurities, (6) wall conditions and (7) tank size. It was found that the number of water guns had relatively little effect. The type of water, the water temperature and impurities in the water and presence of crude oil or sludge on the wall affected the sign and magnitude of the charge, but in an unpredictable way.

In a series of tests on water washing of tanks a typical value obtained for the charge density of the mist was 3×10^{-8} C/m^3. For a 12 m radius tank in the absence of a protrusion this translates using Equation 16.7.57 to a field strength of 13.5 V/m. The field strength at a probe comprising a 2.5 cm cylinder was calculated to be 600 kV/m. The maximum field strength measured was 400 kV/m and the maximum space potential was estimated as 40 kV.

Experiments were conducted to investigate discharges and their incendivity. Tests are described in which a 28 mm hemispherical probe was inserted into a steam mist with a maximum space potential of 36 kV and a field strength of 330 kV/m. Discharges were obtained and were measured as groups of pulses. The discharges were of relatively long duration, some tens of milliseconds, which contrasts with a duration for metal to metal discharges of about 10^{-7} s. The energy dissipation in the first millisecond at this potential was some 0.04 mJ. The author comments that such energy dissipation may be a better measure of incendivity than energy accumulation.

The charging of insulated conductors inside a tank was also studied. The charging mechanisms include charge induction, charge transfer from mist droplets, and corona charging. It was found that with a space potential of 30 kV a cord lowered by a man standing insulated on the deck charged up to about half the space potential within seconds once his resistance to earth exceeded $10^{10}\,\Omega$. A man wearing normal footwear on a well painted deck would have a resistance to earth in excess of this.

In another study a 13 mm diameter rod was dropped through a mist with a maximum space potential of 37 kV and the rod acquired a charge of some 2×10^{-7} C. Laboratory tests showed that such an object could have given an incendive spark.

Smit (1971) describes models for potential distribution developed in support of this work, and Vos (1971) describes work on the generation of a charged mist by an impacting jet, as already described.

J.F. Hughes *et al.* (1973) give an account of related work on water mists. One study dealt with periodic discharges at a probe which were found to be associated with the departure of a water droplet from the probe. These were corona discharges and were not incendive to a propane–air mixture. Another phenomenon investigated was a slug of water falling through the cloud. Slugs of water were made to fall on a trajectory spaced 0.1–0.4 cm from an earthed probe. The discharges obtained were incendive.

A number of mechanisms for incendive discharges in water washing were investigated by van de Weerd (1975), in particular discharges from a falling water slug. Washing machines can give water slugs some 4 cm diameter by 50 cm long. The maximum space potential during tank washing is at least 30 kV. Work was done to determine the fraction of the energy of the charge induced on the slug which participates in the discharge when the slug approaches a protrusion on the tank, and this fraction was estimated as 0.2–0.4. Taking a figure of 0.2 gives a discharge energy of 1.5 mJ. This compares with a minimum ignition energy of some 0.5 mJ for a hydrocarbon–air mixture in this situation. van de Weerd concludes that such discharges are incendive.

H.R. Edwards (1983) addresses the rather different matter of chemical tankers. The background was a proposal to extend to chemical tankers the Safety of Life at Sea (SOLAS) regulations which are applicable to oil tankers. There is a problem with this in that inerting by combustion products is not acceptable for chemicals, whilst the use of nitrogen is expensive.

He describes trials on five chemical tankers in respect of loading, steam cleaning and water washing. It was found that the liquid electrical conductivities were

relatively high, being in the range 20–80 pS/m. These are the conductivities of the industrial chemicals as loaded. For example, Analar quality benzene has a conductivity of 0.8 pS/m, but the conductivity for benzene loaded in the trials was 40 pS/m. The highest value measured for the liquid surface potential was 3.4 kV for benzene. The Carruthers and Wigley model was used to confirm that the liquid surface potential would not give rise to incendive sparks.

In steam cleaning tests the maximum space potential in the steam mist in smaller tanks of 300 m^3 was about 4 kV, but tanks above 1000 m^3 gave potentials above 10 kV, the maximum recorded value being 18 kV.

Edwards details the procedures used in water washing. He gives data on the maximum space potentials in the water mist. Except for esters, the maximum space potential was 7.9 kV. For esters it exceeded 10 kV in several cases, the highest value being 11.7 kV for ethyl acetate. As already described, some of the space potentials given by Edwards are based on his model. He refers to 10 kV as the safety criterion. He lists a number of factors which suggest that, in practice, there is a safety margin. One is the safety margin in the 10 kV criterion itself. Another is the fact that chemical tankers use smaller washing machines, which tend to give smaller water slugs. He suggests that for these the hazard threshold is closer to 15 kV. Another factor is that the maximum space potential is near the centre of the vapour space, which is not the location of protrusions.

The problem of a falling water slug has been investigated further by M.R.O. Jones and Bond (1984, 1985), in the context of chemical tankers. The situation envisaged is a slug falling from the jet of the washing machine and approaching an earthed wall. The authors refer to work by Bustin (1973–74) on the size of water slugs from washing machine jets. They state that the hazardous conditions are often taken to be a space potential of at least 10 kV near the washgun and a slug of at least 0.5 m, but that there is no firm foundation for this.

Jones and Bond refer to the empirical finding of van der Weerd that the effective ignition energy required for a discharge between a water slug and a metal conductor is about twice that for a metal-to-metal discharge. They describe a model for the limiting hazardous conditions in terms of the tank centre space potential (TCSP) and the slug length. They compare their model with data given by H.R. Edwards (1983) on space potential in chemical tankers, described below. The crude data need to be converted to give the TCSP using a suitable model. In their initial work Jones and Bond accept Edwards' model for the calculation of the TCSP, but in the second paper replace this with their own model. The highest TCSP in the test data set is calculated to be some 20 kV. The initial treatment revealed no case in which the safety margin between the observed potential and the hazard threshold value was exceeded, but in some cases the difference was small, whereas in the revised treatment it is considerably larger.

Jones and Bond give a number of recommendations for the conduct of water washing of tanks, including limits on the number of washing machines and the water supply pressure.

J.S. Mills and Haighton (1983) have studied the charging of tanks by the flue gas used for inerting. The charge is generated in the boiler and carried by soot particles. Charge dissipation occurs by drift of soot particles to the walls and by corona discharge. The purpose of the work was to determine whether incendive discharges could be produced and to study the decay of the charge. Tests were done in which discharges from a charged cloud to a projection were simulated by discharges from an electrode. An electrode with a 25 mm diameter tip gave ignition most easily. The lowest space potential at which this electrode would give ignition was estimated as 70 kV. In subsequent ship-board trials the maximum space potential obtained was about 55 kV. The time for decay to 10 kV was about 5.5 hours. It was concluded that the maximum space potentials were not such as to give incendive brush discharges, but that spark discharges from isolated conductors were a possibility and more stringent measures should be taken to exclude these.

J.S. Mills and Oldham (1983) review the hazard of static ignition in tankers. They quote the potentials required to give an incendive brush discharge as 45 kV for a liquid surface potential and 70 kV for the space potential of a mist, both these potentials being negative. They refer to work which has shown mist space positive potentials of 40 kV in open cycle washing and 120 kV in closed cycle washing. These authors also discuss the static hazards of the use of glass reinforced plastic (GRP) pipes in tankers.

16.7.38. Discharges incendive in gas and liquid systems

As far as concerns ignition by an electrostatic discharge, what matters is the incendivity of the discharge. Non-incendive discharges can in some cases be helpful in dissipating charge which might otherwise participate in an incendive discharge. For a discharge to be incendive, a minimum voltage and a minimum energy are required. It is usually reckoned that for a spark discharge from a conducting object into a flammable mixture the minimum voltage is 1000 V, or 1 kV.

As far as the energy of the discharge is concerned, the incendivity of the discharge is generally assessed by comparing the energy of the discharge with the minimum ignition energy (MIE) of the flammable mixture. For a flammable gas or vapour mixture this is the MIE of the gas. For hydrocarbons the figure most often quoted is that for a propane–air mixture which is given as 0.2 mJ. The figure appears to derive in the first instance from Lewis and von Elbe. This MIE is that measured for a spark discharge at metal electrodes. It is effectively a minimum figure.

Certain substances have a lower MIE. Hydrogen and carbon disulphide are the gases generally mentioned in this context. The MIE of carbon disulphide is 0.009 mJ and that of hydrogen is about 0.011 mJ. Substances with such low MIEs are therefore treated as sensitive substances.

In order to assess the incendivity of a discharge, therefore, it is necessary to know any minimum potential required, the energy of the discharge and the efficiency of that energy in effecting ignition relative to the energy in the spark discharge between the metal electrodes used in the measurement of MIEs. For a spark discharge various values are given for the minimum potential, but these often incorporate a safety factor. One commonly quoted value of this kind is 100 V. Britton and Smith

(1988) give a value of 1000 V, or 1 kV, which they relate to the minimum gap required to avoid quenching.

The energy in a spark discharge depends on the potential and on the capacitance of the conductor. The energy is therefore variable, but there are many situations which will give an incendive spark discharge. For a brush discharge a minimum potential is not usually quoted, but may be obtained from field breakdown considerations.

With regard to the energy of a brush discharge use is made of the equivalent energy as proposed by N. Gibson and Lloyd (1965). If a flammable gas has a given MIE and a brush discharge is just able to ignite the appropriate mixture for that gas, the discharge is said to have an equivalent energy equal to the MIE value. Glor quotes values of the equivalent energy of brush discharges in the range 1–3.6 mJ and gives a theoretical treatment for a particular configuration which gives an actual energy of 4 mJ.

A brush discharge is incendive to most flammable gases. A series of studies on brush discharges has been made by Heidelberg (1959, 1967, 1970a).

For a propagating brush discharge there is a minimum voltage across the non-conducting layer for breakdown to occur. This is shown in Figure 16.58 (Maurer *et al.*, 1987). For layers of about 10 μm the minimum voltage is 4 kV, this value rising to 8 kV for layers of about 200 μm.

Other conditions governing propagating brush discharges have been determined by Heidelberg (1967, 1970a), who found that such discharges occur only if the surface charge density exceeds 2.7×10^{-4} C/m^2 and that they do not occur if the non-conducting layer is more than 8 mm thick.

The energy in a propagating brush discharge is very high. It depends essentially on the participating area and the surface charge density. The high energies in propagating discharges may be explained as follows. As explained in Section 16.7.5, the normal maximum surface charge density, given that the permittivity of free space is $\epsilon_o = 8.85 \times 10^{-12}$ F/m, the dielectric strength of air is $\epsilon = 1$ and the breakdown field strength of air is $E_b = 3 \times 10^6$ V/m, is given by Equation 16.7.22 as 2.64×10^{-5} C/m^2. For a configuration capable of giving a propagating brush discharge the relevant quantity to replace the breakdown field strength E_b is the dielectric strength. Then for a typical non-conducting material of dielectric strength 2.7×10^7 V/m and dielectric constant 2–4, the maximum surface charge density becomes 5×10^{-4} C/m^2. This is nearly 20 times the previous figure. A propagating brush discharge is incendive to most flammable gases.

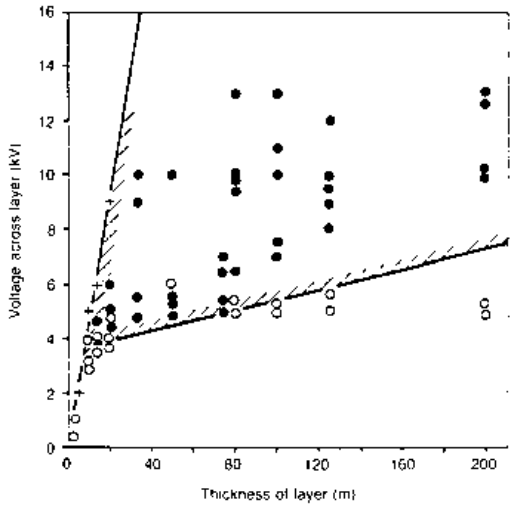


Figure 16.58 *Voltage across dielectric layers for generating a propagating brush discharge: (●) Propagating brush discharges; (○) no propagating brush discharges; (+) breakdown voltage (Maurer et al., 1987) (Courtesy of the Institute of Physics)*

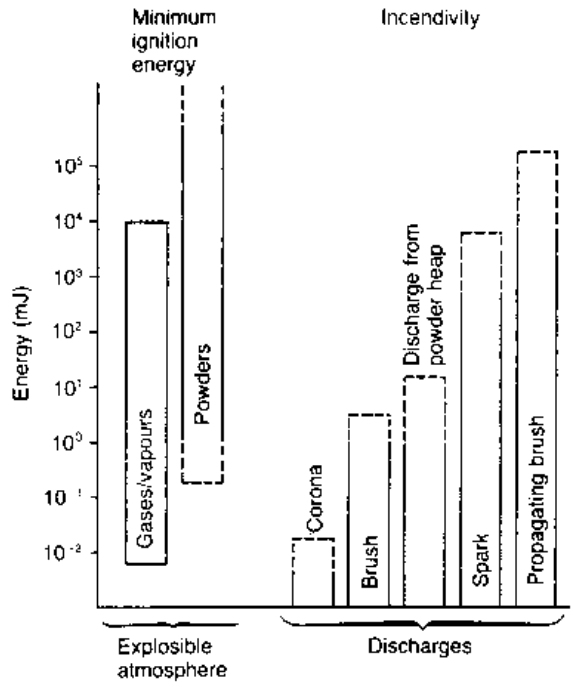


Figure 16.59 *Energy of five types of electrostatic discharge (Glor, 1988) (Courtesy of Research Studies Press)*

The energy in the four main types of discharge and their incendivity to gases and dusts is illustrated in Figure 16.59 (Glor, 1988).

As described in Sections 16.7.27–16.7.39, investigations of liquid storage tanks, road and rail tankers and oil and chemical tankers have often included studies of the incendivity of discharges in these systems. In addition, there has been some work specifically directed to this topic.

In the context of aircraft fuelling, Bruinzeel (1963) carried out experiments on discharges during the filling of a liquid storage tank with kerosene. The tank was 4 × 1 × 0.75 m divided into four compartments. Discharges were observed between the liquid surface and the fill

pipe before its submersion, between the liquid surface and the roof even at a low liquid level, and between the liquid surface and a probe. The discharges occurred most frequently during filling when the liquid level was below one-quarter to one-third full and after it was three-quarters full. The liquid charge when discharges occurred was, with few exceptions, negative.

As found by other workers also, discharges occurred at average field strengths of the order of 400–500 kV/m, although the local field strength at some point must have reached 3000 kV/m. The author quotes, however, the view of Heidelberg and Schön that hazardous discharges might occur at an average field strength as low as 100 kV/m.

Typical results were for a liquid with a conductivity of 3–4 pS/m, a discharge gap of 0.2 m, a charging current of 12–18 μA and a liquid surface potential of 100 kV a discharge energy of 160–500 mJ with more than half being transferred within 0.2–0.3 μs. It was estimated that the charge in the tank was typically 12–18 μC and that in the discharge 1–5 μC. The ignition of a flammable gas mixture was demonstrated.

Leonard and Carhart (1967) carried out work on discharges between the liquid surface of JP4 and JP5 fuels and electrodes of different configurations. These were a needle, a 60° point and $\frac{1}{4}$, $\frac{1}{2}$ and 1 in. sphere electrodes. The characteristics of the discharges between these electrodes and a metal plate were also studied.

The needle and 60° point electrodes gave mainly corona discharges, but the latter also gave spark discharges. The 60° point and small spherical electrodes gave spark discharges at small gaps, but otherwise gave corona discharges. The large spherical electrodes gave pre-breakdown streamers which never made the transition to filamentary sparks. These streamers occurred at a frequency of about 100/min and had a duration some 7 times longer than that of filamentary sparks of the same energy.

It was found that for comparable conditions with the 1 in. spherical electrode the discharges between the electrode and the metal plate had 30–40 times as much energy as those between the electrode and the liquid surface. For the latter case the highest energies, up to 2.3 mJ, were obtained with the 1 in. electrode. The discharges studied were not incendive to JP4.

Summarizing the work on incendive discharges in liquid storage tanks and in road and rail tankers, the principal conditions for which there have been proposed limiting values below which discharges are not incendive are the liquid surface charge and the maximum vapour space potential. For these conditions the value quoted may be either the technical limit at which the discharge is just incendive, or a safety limit which is intended to incorporate a safety margin. Bulkley and Ginsburgh (1968) proposed for the technical limit 20 kV and for the safety limit 10 kV. A much lower figure of 1 kV was suggested for the latter limit by Mahley and Warren (1968). Subsequent workers have regarded this as too low. The technical limit has been proposed as 45 kV by Strawson and Lyle (1975b) and as 25 kV by W.D. Rees (1981). H. Kramer and Schön (1975) have proposed 35 kV as the technical limit on the maximum vapour space potential.

As far as concerns tanker water washing, a technical limit for the maximum vapour space potential of below 37 kV emerges from the work of van de Weerd (1971), whilst one of 70 kV has been given by J.S. Mills and Oldham (1983). The safety limit on the maximum vapour space potential is taken as 10 kV by H.R. Edwards (1983) and by M.R.O. Jones and Bond (1984, 1985).

16.7.39 Powders and dusts

The problem of ignition by static electricity in powder handling has some similarities with that in handling liquids, but there are also some important differences.

The powder may be handled as a dust suspension or a settled powder, and often as both.

The charging tendency of a powder is difficult to predict, but it tends to be high. It is also difficult to modify. Options which can be used with liquids may not be available. There is limited scope for reducing the velocity in pneumatic conveying. There is also limited scope for dosing with an additive to increase conductivity.

In the settled state particularly, a powder has a high bulk density and its volume charge density tends to be correspondingly high.

Prediction of the charging tendency is made difficult by a number of factors, including the particle diameter and size distribution, impurities, the water content, and the speed of separation.

The extent of charging of a powder depends on its volume resistivity. Charging is to be expected at a resistivity of $10^8\,\Omega$m and above. The resistivity of most organic powders exceeds this value.

Some data on the electrical volume resistivity of powders are given in Table 16.37. Figure 16.60 (N. Gibson, 1971) shows the distribution of the resistivities of organic powder products.

Given that the resistivity of the powder is sufficiently high for it to exhibit charging, the charging tendency depends more on the operations to which the powder is subjected than on the powder properties. Operations in which charging occurs include micronizing, grinding, sieving, gas filtration, pneumatic conveying and mechanical transfer.

The electrostatic charges generated in powders by these operations are typically as follows (N. Gibson, 1969):

	Charge (C/lb)
Micronizing	10^{-7}–10^{-3}
Grinding	10^{-7}–10^{-6}
Scroll feed transfer	10^{-8}–10^{-6}
Pouring	10^{-9}–10^{-7}
Sieving	10^{-11}–10^{-9}

The charge per particle increases, but less than proportionately, with increasing particle diameter. Thus the charge per unit mass must decrease. This is in line with the data just given.

The charge density on a powder is commonly expressed either as the volume charge density or the mass charge density. The relation between the two is

$$\frac{q}{m} = \frac{s}{\rho_e} \qquad [16.7.226]$$

Table 16.37 *Electrical volume and surface resistivity of selected solid materials*

A Volume and surface resistivity[a]

	Volume resistivity[b] (Ω m)	*Surface resistivity*[c] (Ω)
Plastics, overall range	$10^6 - 10^{15}$	$10^8 - 10^{17}$
PVC, unplasticized	$10^{12} - 10^{13}$	$10^{13} - 10^{14}$
PVC, plasticized	$10^9 - 10^{12}$	$10^{10} - 10^{13}$
Polyethylene, high density	10^{14}	$10^{14} - 10^{15}$
Polyethylene, low density	10^{15}	$10^{14} - 10^{15}$
Polypropylene	10^{15}	$10^{14} - 10^{15}$

B Surface resistivity of glass: effect of relative humidity[d]

Relative humidity (%)	*Relative surface resistivity*
100	1
80	4
70	30
60	800
50	30 000
40	6 000 000

[a] Source: Lüttgens and Glor (1989).
[b] Manufacturer's specification.
[c] Literature values.
[d] Source: W.F. Cooper (1953b), quoting Smail, Brooksbank and Thornton (1931).

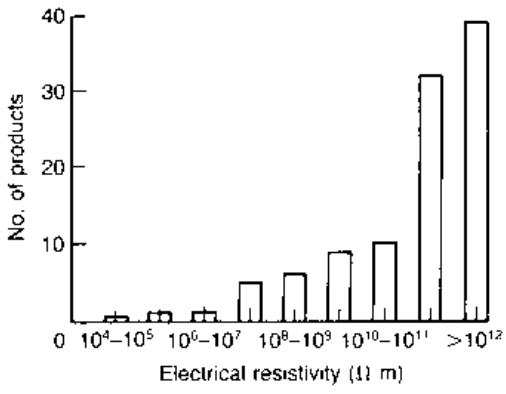


Figure 16.60 *Electrical volume resistivity of powders (N. Gibson, 1979) (Courtesy of* Filtration and Separation*)*

where q is the charge on a particle (C), m is the mass of the particle (kg), s is the volume charge density (C/m^3) and ρ_e is the effective density (kg/m^3 air). The ratio q/m is also the mass charge density of the powder (C/kg). The effective density is that of the dust cloud or settled powder, as the case may be, and in the latter case it is the bulk density.

The charge on a particle is then

$$q = \pi d^2 \sigma \qquad [16.7.227]$$

the mass is

$$m = \frac{\pi}{6} d_d^3 \rho_s \qquad [16.7.228]$$

where d_d is the particle diameter (m) and ρ_s is the density of the particle (kg/m^3). Hence from Equations 16.7.227 and 16.7.228

$$\frac{q}{m} = \frac{6\sigma}{d_p \rho_s} \qquad [16.7.229]$$

The maximum charge on the particle in free space is determined by the maximum surface charge density.

As an illustration, consider a powder with a material density of 1000 kg/m^3 and a limiting surface charge density in free space of 2.7×10^{-5} C/m^2. Then for particle diameters of 10^{-2} and 10^{-6} m Equation 16.7.229 gives mass charge densities of 1.6×10^{-5} and 2×10^{-1} C/kg, respectively.

Dust may be in suspension or deposited. There is very little information on the occurrence of discharge between particles in suspension, but it cannot be ruled out. With a deposited dust there is a relaxation of the charge similar to that in a liquid. If the dust has a high resistivity, the relaxation time may be hours or even days. Discharges from deposited dusts are often coronas.

In much equipment handling dusts a flammable atmosphere does not exist during normal operation, because the dust suspension is above its upper flammability limit. But a flammable suspension is more likely to occur during transient conditions such as start-up and shut-down.

The principal hazard in dust-handling equipment is that presented by a container or other object made of conducting material but insulated from earth. There are certain factors which tend to reduce the probability of electrostatic ignition in equipment handling dust suspensions. One is that the dust suspensions tend to have high minimum ignition energies. A second is that

discharge is frequently by a corona. The hazard of static electricity in dusts is discussed by K.N. Palmer (1973a).

16.7.40 Powder flow in pipes

The charging current for the flow of particles in a pipe, in other words in pneumatic conveying, has not been studied as extensively as that for liquids. The most common approach appears to be to estimate the maximum theoretical charge on the particles and to express the experimental results in terms of the fraction of this maximum charge attained.

The maximum charge on a particle in flow in a pipe differs from the maximum charge in free space. The maximum space charge density is obtained from Equation 16.7.61 and is inserted in Equation 16.7.229 to give the maximum charge on a particle q/m, or mass charge density.

As an illustration, consider the example given by J.F. Hughes and Bright (1979) for which the pipe radius is 0.05 m and the particle density is $0.95 \times 10^3\,\mathrm{kg/m^3}$. Then, utilizing the usual values for the permittivity of air and the breakdown field strength, Equation 16.7.61 gives a space charge density of about $1.06\,\mathrm{C/m^3}$ and Equation 16.7.229 gives a mass charge density of about $1.12 \times 10^{-6}\,\mathrm{C/kg}$. Furthermore, by equating the mass charge density q/m in Equations 16.7.226 and 16.7.229, and utilizing Equations 16.7.22 and 16.7.61, the condition for the equality of the maximum mass charge densities in free space and in a pipe is obtained:

$$\frac{d_\mathrm{d}\rho_\mathrm{s}}{3r_\mathrm{p}\rho_\mathrm{e}} = 1 \qquad [16.7.230]$$

Several workers have obtained experimentally determined values of mass charge densities, and hence charging currents, which are close to the theoretical maximum. For example, J.F. Hughes and Bright (1979) report mass charge densities of $0.8\text{–}3.4 \times 10^{-6}\,\mathrm{C/kg}$ for the case described above, for which the theoretical value was $1.12\,\mathrm{C/kg}$. On the other hand, Boschung and Glor (1980) obtained the results shown in Figure 16.61, where the experimental mass charge densities are about one-tenth of the theoretical values.

16.7.41 Powder storage silos

As with liquid storage tanks, so with powder silos there is a problem of charge accumulation and relaxation. The heap of powder in a silo tends to have a high volume resistivity and a high mass charge density. Such a powder will therefore retain a large charge over a long period. Relaxation of the charge may take days or even weeks.

The main hazard in such a situation is a discharge. The envelope of conditions which can give a discharge is determined by two limiting factors. The field must be strong enough to give field breakdown but not so strong that it prevents a charged particle from settling under gravity. Glor (1984) has utilized these two limitations to derive a simple model which gives the envelope for discharges shown in Figure 16.62. This model leads to the conclusion that discharges are to be expected only for rather coarse powders, having particle diameters in the range 1–10 mm.

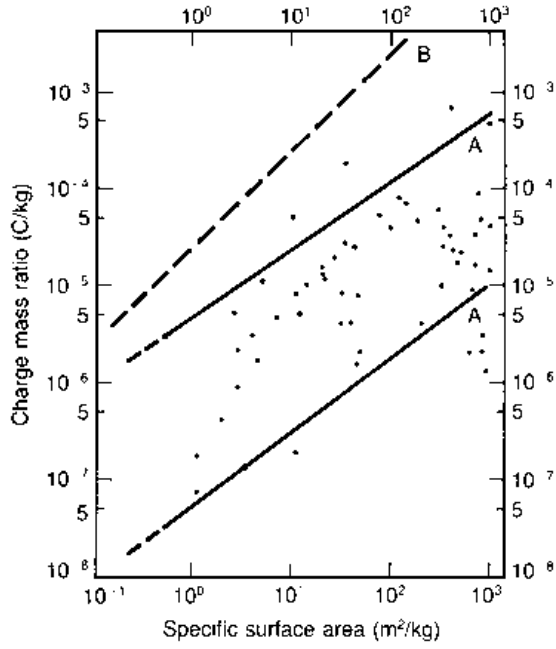


Figure 16.61 *Mass charge densities in powder flow in a pipe (Boschung and Glor, 1980): A, general trend of experimental data; and B, maximum values from a theoretical model (Courtesy of the* Journal of Electrostatics)

16.7.42 Discharges incendive in powder and dust systems

The incendivity of discharges for flammable gases was described in Section 16.7.10. The incendivity of a discharge for dusts may be determined by comparing the effective energy of the discharge with the MIE of the dust. The MIEs of dusts are given in Chapter 17 but, broadly, dusts typically have an MIE in the range 1–10 mJ.

A spark discharge may be incendive to dusts, depending on its energy.

A brush discharge is not regarded as incendive to dusts. According to Glor, there is no known case of ignition of a dust by a brush discharge. In practice it is difficult in handling powders to avoid brush discharges.

A propagating brush discharge has very high energy and is incendive to most dusts.

With powders it is also necessary to consider another type of discharge, i.e. a bulking brush discharge in a silo. A discussion of the conditions under which such a discharge is most likely to occur has been given by Glor (1988). The conditions are a high bulk resistivity ($>10^{10}\,\Omega\,\mathrm{m}$) and relatively large particle size (diameter $>$ 1 mm). The energy release in a bulking brush discharge is estimated to be of the order of 10 mJ and this is sufficiently high to be incendive to many dusts.

16.7.43 Drums and small containers

As mentioned earlier, explosions due to static ignition also occur in the filling of drums. Treatments of this

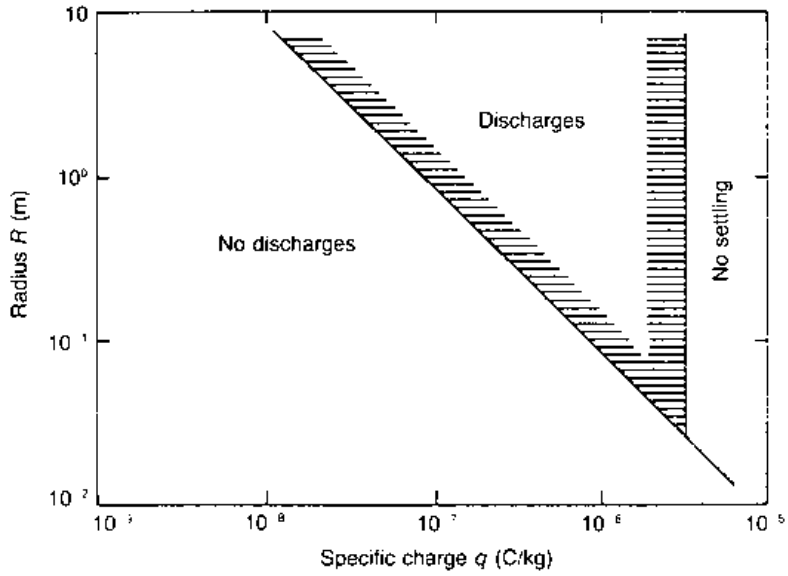


Figure 16.62 *Region for brush discharges on a settled powder in a silo: spherical heap of radius R (Glor, 1984) (Courtesy of the* Journal of Electrostatics*)*

problem include those by Pesetsky and Fisher (1975), Britton and Smith (1988) and Rosenthal (1988).

An incident is described by Pesetsky and Fisher involving an explosion during the filling with toluene of a 55 USgal steel drum which was not earthed. The drum was lined with a 5 mil (1 mil = 0.001 in) non-conductive epoxy coating. Tests showed that when an unearthed steel drum was filled with toluene, discharges between the steel drum and an earthed probe regularly caused ignition. It was also found that insertion of a 3 ft section of plastic pipe into the filling line increased the charging current by a factor of 23. It was estimated that under the test conditions the capacitance of the drum was about 100 pF, whilst the potential was measured as 8700 V, giving an energy of 3.6 mJ. In other tests in which a plastic drum and a plastic filling pipe were substituted, both the drum and the liquid reached a potential of 87 000 V, i.e. a value 10 times as high, but incendive discharges were not obtained between an earthed probe and the liquid surface. The authors refer, however, to work by Bruinzeel (1963) on tank filling, using a liquid with a conductivity some 20 times less than toluene, in which incendive discharges were obtained from the liquid surface.

Britton and Smith (1988) describe an extensive investigation of drum explosions, following an incident in which an explosion occurred in a lined drum which was earthed. A review of all available incidents showed that in all cases low conductivity liquids (<50 pS/m) were involved. The authors conclude, however, that in certain situations an incendive discharge may be given by a conductive liquid. Whilst it is true that for an earthed drum, unlined or with a lining of negligible resistance, an incendive discharge requires a low conductivity liquid, with a lined drum it may occur with either a conductive or a low conductivity liquid.

In at least one case reviewed the drum was earthed and the ignition occurred due to brush discharge between the liquid surface and the filling lance tip. It is this type of incendive discharge in particular that the authors address.

Such a discharge has a relatively low energy and ignition occurs only over a limited range of concentration. This cuts both ways. On the one hand it greatly reduces the risk of an explosion, but on the other it means that the fact that an explosion has not occurred to date is no guarantee that it will not do so.

The risk of static ignition depends on a number of factors, including the earthing, the drum, the liquid conductivity, the filling arrangements and the fill pipe. With regard to earthing, the authors state that to obtain an incendive discharge a potential of 1000 V is required. Allowing a safety factor of 10, the potential should be limited to 100 V. The charging current rarely exceeds 10^{-4} A. Thus it is sufficient that the resistance to earth does not exceed 1 MΩ.

One measure is to reduce the resistance of the lining. Some drum linings have a significant electrical resistance, while others do not. Polyethylene, for example, is essentially a perfect insulator. On the other hand, drum coatings of the epoxy or phenolic types have very low resistance.

Another approach is to address the charge generation and relaxation. Some features are prolific charge generators. The authors state that a high charging current can be generated not only by a filter but also by a hose with an internal earthing spiral. In their work, such a hose gave a charging current much greater than that of

a smooth bore hose and within an order of magnitude of that produced by a microfilter.

Britton and Smith refer to recommendations on relaxation of the charge. It is normally advised that three time constants be provided for the liquid between a filter and the drum. Of the then current guides, API RP 2003 gives a relaxation time of 30 seconds for liquids with a conductivity less than 50 pS/m, and BS 5958:1991 gives a relaxation time of 3 time constants for liquids with conductivities down to 2 pS/m combined with a global relaxation time of 100 seconds for liquids with lower conductivity.

The design of the fill pipe is also important. The dip pipe should have the largest practicable diameter and should have a pointed end; a rounded end is to be avoided.

The authors present electrostatic models for drums in support of the assessment of the risk of incendive discharge.

Dahn, Kashani and Reyes (1994) describe the problem of control of the static electricity hazard in the use of flexible intermediate bulk containers (FIBCs) for powders. They point out the hazard of attempting to solve the problem by utilizing earthed exterior bag surfaces. This tends to increase the likelihood of a propagating brush discharge. Further, if the earthing is lost and the static charge is high, there is potential for an incendive discharge.

They describe their preferred approach, the elements of which are to estimate the static charging rate, the charge dissipation rate, the field strength and the discharge strength. The charging rate is determined by a test in which the powder is passed down an inclined chute into a metal bucket container where the charge is measured. Tests are also done using an ASTM method to determine the surface and volume resistivities so that the charge dissipation may be estimated.

For the field strength in the container they use Equation 16.7.58a. As an illustration, they give a calculation of the field strength for the case of a container of radius 0.807 m, with a charge density of 38.53×10^{-6} C/m^3 and utilizing the permittivity of air of 8.83×10^{-12} C/V m. The resultant field strength is 1171 kV/m.

They also give calculations of the energy in a propagating brush discharge.

16.7.44 Moving machinery

Static electricity is generated by the relative movement of surfaces in machinery. In particular, conveyor belts and reeled material tend to accumulate a large electrostatic charge.

The voltages generated by a conveyor belt are often compared with those generated by a van de Graaff generator. Typically such a generator might have a potential of 100 kV with a current of several microamps, but values of up to 50 kV and several milliamps have been quoted.

Cross (1981) has described experiments on two conveyor belts, one an insulating belt and one an antistatic belt, in which the effect of humidity was measured. At zero absolute humidity the potential on the insulating belt reached 110 kV, whilst that on the antistatic belt was about 6 kV. Bucket elevators also can build up an appreciable charge.

16.7.45 Human body

The human body can become electrostatically charged and can be the source of an incendive spark. The human body has a low volume resistivity and thus acts as a conductor. Charging can occur by contact charging, by induction or by charge sharing. Some activities which can cause charging are walking, rubbing, removing clothing, pouring liquids and powders, and touching charged objects. The maximum potential of the body is of the order of 50 kV, the limitation being leakage and sparking. It is not uncommon for the body to be at some 10 kV. The capacitance of the body is in the range 100–300 pF, say 200 pF. Then at a potential of 10 kV, from Equation 16.7.19 the energy of a discharge from the body is some 10 mJ.

Discharge from the body is therefore capable of giving a spark incendive to a flammable gas mixture. Removal of clothing can also give an incendive spark. BS 5958:1991 recommends precautions against incendive discharge for the body for flammable mixtures with MIEs $\leq$ 100 mJ. Discharge from clothing is reckoned to be incendive only to sensitive mixtures.

The main precaution against sparks from the human body is earthing. The charging current which occurs as a result of manual activities generally does not exceed 10^{-6} A. Then, applying the $100/I$ criterion gives a required resistance to earth of not more than $10^8\,\Omega$. There are also two other relevant criteria. For avoidance of uncomfortable shocks the resistance to earth should not exceed $10^9\,\Omega$. For protection against mains voltage it should not exceed $5 \times 10^4\,\Omega$. In BS 5958 Part 1: 1991 a resistance to earth for personnel of 10 Ω represents good practice in most applications, but the standard allows one of up to $10^6\,\Omega$ in certain cases.

In order to achieve this degree of earthing it is necessary to consider both footwear and flooring. BS 5958:1991 gives requirements for the two main types of footwear used: antistatic footwear and conducting foot wear. It also states that leather footwear usually has a sufficiently low resistance, except when very dry.

BS 2050:1978 gives requirements for flooring materials and BS 3187:1991 gives requirements for laid floors, but only of the conductive type. A conductive type floor is not suitable if protection is required against mains voltage. It is sometimes permissible to provide a limited area of low resistance flooring such as a metal plate.

16.7.46 Containments

The effect of the containment has been referred to a number of times in the preceding sections. It is now considered in more detail. Containment materials are classed as conductive or non-conductive. BS 5958:1991 defines a non-conductive, or high resistivity, material as one with volume and surface resistivities of $10^{12}\,\Omega$.m and $10^{12}\,\Omega$, respectively. In process containments the principal conductive materials are metals and the principal non-conductive materials are plastics. Some data on the electrical volume and surface resistivities of solid materials are given in Table 16.37. In addition, use is also made of non-metallic conductive materials, essentially plastics modified to increase their conductivity.

Some principal containments and containment materials are given in Table 16.38, based broadly on the distinctions made in BS 5958. Most are self-explanatory, but several require further comment. Where the

Table 16.38 *Some containments and containment materials*

Metal container for liquids
Non-conducting container for liquids
Metal container for liquids with fixed non-metallic coating
Metal container for liquids with outer non-metallic coating/jacket
Metal pipes for gases and liquids
Metal container for powders
Non-conducting container for powders
Container for powders with liner:
Metal container with conductive liner
Metal container with non-conductive liner
Non-conductive container with non-conductive liner

container is non-conducting, there may be the possibility of a discharge from its external surface. Some metal containers have an internal non-conductive coating. This creates the possibility that charge from repeated filling or rubbing is retained on the coating. Metal containers may also have an external non-conductive coating or jacket. There is then the possibility of a discharge from the external surface of the container. Another possible effect where there is a non-conductive outer surface, whether that of the main container or of a coating, is that metallic objects on this surface may constitute isolated conductors. Any situation where there may be a discharge from the container is relevant if the container is in a classified hazardous area.

Some containers for dry powders have removable liners. Broadly, BS 5958:1991 treats a metal container with a conductive liner as an unlined metal container and a non-conductive container with a non-conductive liner as an unlined non-conductive container. It recommends against the use of a non-conductive liner with a metal container or of a conductive liner with a non-conductive container, and recommends additional precautions where such mixed systems have to be used.

16.7.47 Precautions against static electricity

Static electricity can act as a source of ignition giving rise to a fire or explosion only under the following conditions:

(1) a flammable atmosphere exists;
(2) an electrostatic charge is generated, accumulates and produces an electric field strength which exceeds the critical value for breakdown;
(3) the resultant incendive discharge has an energy greater than the minimum ignition energy of the flammable atmosphere.

Thus precautions against static electricity aim to eliminate one or more of the above factors. These precautions tend to be based, therefore, on the following approaches:

(1) elimination of a flammable atmosphere;
(2) control of charge generation;
(3) control of charge accumulation;
(4) minimization of incendive discharge.

It is a general principle in handling flammable materials to make avoidance of a flammable atmosphere the first line of defence where this is practical. It is necessary also to try to eliminate sources of ignition, but it is much more difficult to do this reliably.

Since electrostatic charge builds up both on process materials and on process plant, it is not sufficient simply to ensure that charge is drained away from plant by measures such as earthing. It is essential to deal also with the charge on the material being handled.

In the handling of liquids the precautions used may include the following:

(1) elimination of flammable mixtures;
(2) bonding and earthing;
(3) modification of liquid conductivity;
(4) limitation of flow velocity;
(5) minimization of charge generation by –
  (a) immiscible liquids,
  (b) filters, valves;
(6) avoidance of splashing and settling;
(7) avoidance of earthed probes;
(8) earthing of personnel;
(9) measures associated with low conductivity containers;
(10) provision of relaxation time.

The elimination of a flammable mixture is used particularly for liquid storage tanks and for tank cleaning on tankers.

Bonding and earthing are discussed in Section 16.7.48.

The modification of liquid conductivity was developed particularly by Shell, and the Shell additive ASA 3 is widely used for conductivity modification. Modification of liquid conductivity has been discussed by Klinkenberg and van der Minne (1958). The liquid conductivities recommended in order to keep charge separation below a safe level are 50 and 500 pS/m for pipeline velocities below and above 7 m/s, respectively.

Thus some products, such as crude oil, have a sufficiently high conductivity to render them safe, while others, such as light distillates, do not. It is possible, however, to modify the conductivity of the latter by the use of a very small amount of a suitable additive. Additives are usually a combination of divalent or polyvalent metal salt of an acid such as carboxylic or sulphonic acid and a suitable electrolyte that imparts a conductivity of about 10 000 pS/m in a 0.1% solution in benzene. Thus concentrations of 0.6 and 6 ppm of additive Shell ASA 3 raise the conductivity of such products to about 200–300 and 1000 pS/m, respectively.

The charging current in the pipeline flow of liquids is of the order of 10^{-10}–10^{-7} A. This current is approximately proportional to the square of the velocity. Charge generation can therefore be reduced by keeping the velocity down. A limit on pipeline velocities of 7 and 1 m/s, respectively, for liquids without and with an immiscible component has been recommended by Klinkenberg and van der Minne (1958). The much lower limit for liquids with an immiscible component, such as free water, is due to the fact that in such liquids the rate of charge generation can be up to 50 times greater.

Filters generally require special precautions. Since the streaming current generated in a filter is proportional to the flow rate rather than the square of the flow rate, as with a pipe, the limitation of liquid velocity is rather less effective for filters. The usual approach is to allow a

relaxation time by providing an adequate length of pipe between the filter and the tank. This is more difficult to do, however, for high purity products with long relaxation times.

For liquid storage in a tank of non-conductive material or in a tank of non-conductive material with an embedded metal grid not in contact with the liquid, BS 5958:1991 recommends the use of an earthing plate of area

$$A_{ep} = 0.04V_t \qquad [16.7.231]$$

where A_{ep} is the area of the earthing plate (m^2) and V_t is the volume of the tank (m^3).

Although they are generally less prolific generators than filters, valves and other constrictions can also give substantial increases in charging.

Tank filling arrangements should avoid free fall and splash filling of liquids. Inlets should reach to the bottom of the tank or, preferably, should enter at the bottom of the tank and be submerged.

Earthed probes in tanks should be avoided as far as is practicable, as should isolated conductors.

There should be suitable arrangements for level gauging. The hazard is reduced if antistatic additives are used and if an adequate relaxation time is allowed. Level measuring equipment which is used where there is an electrostatic hazard includes non-conducting ullage tapes and permanently fixed and earthed sounding pipes extending to within a few centimetres of the tank bottom. Detailed discussions of the precautions associated with level gauging are given by J.R. Hughes (1970) and Page and Gardner (1971).

Settling of immiscible liquids, such as water droplets in oil, should be avoided as far as possible.

A liquid storage tank made of a non-conductive material may be provided with an earthed metal grid on or just below the surface throughout the material. If this conducting grid covers the inner surface of the tank and is thus in contact with the liquid, this provides an earth for the liquid.

Precautions against the charging of the human body take the form of special footwear and flooring. There are two types of product available: antistatic and conductive. Both prevent accumulation of electrostatic charge, but whereas the former gives protection against electrical mains failure, the latter does not and should only be used where there is other protection against such failure. There are a number of British Standards on antistatic and conductive footwear and flooring. Since the resistance of these products can change, it is important that it be monitored regularly; instruments are available to do this.

The hazard involved in using non-conducting containers may be dealt with by limiting the container size. Some maximum sizes for non-conducting plastic containers have been suggested by Heidelberg and Schön (1960) as follows:

	Maximum container size (l)
Liquids with low ignition energy	1
Liquids with flashpoint <21°C	2–5
Liquids with flashpoint >21°C	60

As already indicated, both conducting and non-conducting containers present static electricity hazards and applications need to be considered individually.

The precautions required in the handling of dusts and powders are somewhat similar to those for liquid handling. Principal measures again include elimination of flammable suspensions, bonding and earthing of plant, and earthing of personnel. Antistatic additives which modify dust resistivity are not well developed. Measures such as humidification and ionization are used, but have limitations. Non-metallic containers for sensitive dusts should have low resistance. Detailed information on the precautions for dust handling are given by K.N. Palmer (1973a).

The electrostatic hazard from steam leaks is that a nearby conductor insulated from earth becomes charged. An example of such a conductor is wire netting around lagging. Insulated conductors should be avoided in situations where they could become a hazard.

Steam used for purging or cleaning can cause charge generation. Again it is necessary to consider both the plant and the fluid. The risk of unearthed pipelines and charge accumulation on these is reduced if the lines used are fixed rather than portable apparatus. Charge generation in the steam should be minimized by keeping the flow velocity down. Earthed probes should be avoided so that the probability of a discharge is reduced.

Carbon dioxide should not be used for the rapid inerting of flammable atmospheres, since it can generate static electricity and so act as an ignition source.

The accumulation of electrostatic charge on moving machinery can be prevented in some cases by earthing the machinery. Objects such as conveyor belts and transmission belts, however, may also accumulate charge and this is not prevented by normal earthing arrangements. The usual solution is to modify the conductivity of the belt material by the incorporation of additives during manufacturing or by the use of a dressing in operation.

The reduction of the resistance of materials is a widely used approach and there are British Standard specifications for low resistance polymeric materials not only for flooring, footwear and belts, as already mentioned, but also for sheeting, hose, tyres and wheels.

Electrostatic eliminators based on ionization are used to prevent charge accumulation in applications such as reeling operations. The charge is either drained to earth through the ionized air or is directly neutralized by ions from the air. Air can be ionized by heat, high voltage, ultraviolet light or radioactivity. Not all types of electrostatic eliminator are suitable for flammable atmospheres. Flames are sometimes used, for example, as ionizers on printing presses.

Devices which have pointed surfaces and are electrically energized are another type of ionizer. If flammable mixtures can be present, however, it is necessary to ensure that the electrical equipment is not itself a source of ignition.

Another method of ionization uses a radioactive source. This type of equipment is of limited applicability, because it is only suitable where charging rates are low. It is used, however, in the paper and textile industries. It is necessary with such devices to take the usual precautions for a radioactive hazard.

Since a pointed object will ionize air near a charged object, it is also possible to use devices rather like wire brushes as induction collectors. There is in this case no electrical energization.

The relative humidity in the atmosphere has a considerable influence on the incidence of electrostatic hazards. In general, most fires attributed to static electricity occur indoors in winter when the relative humidity is below about 30%. If the relative humidity is kept above 60–70%, the electrostatic charge tends to drain away. This is largely a surface electrical conductivity effect. The change in surface conductivity with relative humidity can be dramatic. For plate glass there is a 1000–fold increase in surface conductivity between 20% and 50% relative humidity.

16.7.48 Precautions against static electricity: earthing and bonding

Earthing and bonding comprise one of the principal methods of providing protection against static electricity. Bonding involves making an electrical connection between two conducting objects and earth. The effect of bonding is to maintain the two objects connected at the same potential and that of earthing is to drain away to earth the charge on the object connected. Earthing and bonding systems are also required to give protection against electrical systems and against lightning, but the systems considered here relate only to static electricity.

The purpose of earthing and bonding is to prevent an incendive discharge. The conditions for an incendive discharge to occur are that the field strength reaches the breakdown value and that the energy in the discharge equals the relevant ignition energy.

A potential of at least 300 V is normally considered necessary for an incendive discharge, but since a potential of 100 V has been considered hazardous in explosives manufacture, the latter figure is generally taken as the limit value. Applying Equation 16.7.1 (Ohm's law) gives the criterion that the resistance should not exceed $100/I$. Charging currents vary in the range 10^{-11}–10^{-4} A. Taking the worst case of a charging current of 10^{-4} A yields the criterion resistance to earth of $10^{6}\,\Omega$. Taking a more realistic value of 10^{-6} A for the charging current yields a resistance to earth of $10^{8}\,\Omega$.

As a practical matter it is usually recommended that for conducting equipment, such as a metal, the resistance to earth should not exceed 10 Ω. The reason for this is that the equipment might contain certain high resistance features such as paint, grease and oil, corrosion and rust, which could increase in resistance and negate the required earthing if the resistance were set at, say, $10^{6}\,\Omega$. The value recommended in BS 5958:1991 is 10 Ω; this has the advantage of being the same as the value prescribed for lightning protection.

Different requirements for earthing are given in BS 5958 for equipment made of non-conducting material and of conductive or antistatic materials. For plant built in non-conducting material, isolated conductors are of particular concern. It is frequently recommended that all isolated conductors be earthed. BS 5958 questions this philosophy and proposes instead an approach based essentially on hazard assessment, taking into account the probability that the item will be charged, that it will give an incendive spark and that a flammable mixture will be present.

For equipment made of conductive or antistatic material, BS 5958 recommends a resistance to earth not greater than $100/I$. This will tend give a resistance in the range 10^{4}–$10^{8}\,\Omega$. The general recommendation is for $10^{6}\,\Omega$, but a higher resistance which still meets the $100/I$ criterion is acceptable.

General earthing requirements are discussed in BS 5958: Part 1: 1991. These include a table summarizing the requirements. Further guidance on detailed requirements for particular situations is given in BS 5958: Part 2: 1991.

Earthing is usually effected by means of copper strips or wire attached to a special point on the object to be earthed. Bonding across flanged joints to ensure better electrical continuity than that through the bolts has been widely practised, but many companies have satisfied themselves by tests that this is not necessary and have discontinued the practice.

A good earthing system also requires that it be recognizable as such and that it be checked periodically and after maintenance operations.

Earthing of the human body and the use of appropriate footwear and floors is described in Section 16.7.45.

16.7.49 Precautions against static electricity: BS 5958

BS 5958: Parts 1 and 2: 1991 gives very detailed recommendations for precautions against static electricity, with those for particular situations being given in Part 2. Table 16.39 lists the principal contents of Part 2.

Some of the precautions for handling liquids recommended in BS 5958: Part 2: 1991 are summarized in Table 16.40. For liquid storage tanks made of metal, a flammable atmosphere may be eliminated by reduction of the vapour space by using a floating roof, or by some form of atmosphere control such as inerting. The tank should be earthed. Splash filling should be avoided. Filling may be by a top or bottom fill pipe. A top fill pipe should extend close to the bottom of the tank. There should be a limitation of the liquid velocity during filling. Measures should be taken to avoid excessive charge in the liquid entering the tank. An adequate relaxation time should be allowed before operations such as gauging and sampling are carried out. Measures should be taken to avoid discharge between the liquid in the tank and the tank itself during such operations.

The Standard discourages the use of non-conductive liquid storage tanks and recommends that specialist advice be taken before installing one. The precautions recommended for metal storage tanks apply, but in addition it is preferable that the liquid itself should be earthed and, for a classified hazardous area, the effect of an external discharge should be considered.

The recommendations for metal road and rail tanks are broadly similar, but additional measures are specified concerning filling hoses.

For barge and ship loading BS 5958: 1991 gives recommendations on atmosphere control, earthing, fill pipes and liquid filling velocity.

Some of the limitations on liquid velocity for operations involving filling with liquids, as given in BS 5958: 1991, are summarized in Table 16.41. For small liquid containers the Standard recommends for metal containers earthing of the container and a limitation of the liquid velocity during filling. For non-conductive containers consideration needs to be given to the hazardous area

Table 16.39 *Principal contents of BS 5958: Part 2: 1991*

Larger containers
3. Fixed metal tanks for the storage of liquids
4. Fixed non-metallic tanks for the storage of liquids sited partially or wholly above ground
5. Fixed non-metallic tanks for the storage of liquids sited completely below ground
7. Metal road/rail tanks for liquids
8. Non-metallic road/rail tanks for liquids
13. Ships (tankers) and barges
17. Metal containers and tanks for the storage and transport of liquids, with a fixed internal non-metallic coating
18. Metal containers for liquids with outer non-metallic coatings or jackets

Smaller containers
11. Small metal containers for liquids
12. Small non-metallic containers for liquids
21. Containers for powders
22. Flexible intermediate bulk containers
23. Removable non-metallic liners in containers for solvent wet materials or powders

Equipment and processes
9. Installation for the transfer of liquids to and from road and rail vehicles
10. Liquid/liquid and solid/liquid blending and mixing
16. Fine particle filters and water separators
19. Pipelines for liquids and gases
20. Pneumatic conveying systems
33. Vacuum filters
34. Centrifuges
35. Flaker
36. Dust collectors

Operations
6. Gauging and sampling of tanks
14. Tank cleaning with high pressure water jets or steam
24. Manual addition of powders to flammable liquids
25. Release of gases and vapours

classification. The container itself can be considered a Zone 1 area if either a flammable liquid is being handled or if a flammable atmosphere may be present in normal operation. A non-conductive container should be used only if the risk of ignition is acceptably low, which may be a matter for expert guidance. With non-conductive containers in classified hazardous areas consideration needs to be given also to external discharge. This applies whether or not the liquid is flammable.

The standard also gives precautions for filling containers with high resistivity powders. These may be summarized as follows. A distinction is made between metal containers of volume $\leq 65\,m^3$ or non-metallic containers of $5\,m^3$ and larger ones, and between powders which give rise to flammable mixtures with a minimum ignition energy (MIE) of $\leq 25\,mJ$ and those with an MIE of $> 25\,mJ$. It may be noted that for metal containers the volume delimitation just quoted is an increase from one of $5\,m^3$ in the 1983 edition, reflecting a growth in knowledge. For metal containers, if the container volume is $\leq 65\,m^3$ and the MIE is $> 25\,mJ$, the measures recommended are to earth the container and any filling pipe. However, if there is a possibility that a flammable atmosphere such as a dust cloud with an MIE of $\leq 100\,mJ$ could occur, personnel should also be earthed. For the same size container, if the MIE is $\leq 25\,mJ$, there should be earthing of equipment and personnel and, in addition, consideration should be given to charge rate limitation and explosion prevention and protection; these comprise a set of measures which in this context it is convenient to refer to as 'explosion protection'. If the metal container is $> 65\,m^3$, there should be earthing of equipment and personnel and, unless incendive discharges can be ruled out, consideration should be given to explosion protection. Moving on to non-metallic containers to be filled with dry powders, if the container volume is $\leq 5\,m^3$ and the MIE is $> 25\,mJ$, the measures recommended are to earth the container and any filling pipe. It should also be established that the rate of charge input is insufficient to promote propagating brush discharges. However, if there is a possibility that a dust cloud with an MIE of $\leq 100\,mJ$ could occur, personnel should also be earthed. For the same size container, if the MIE is $\leq 25\,mJ$, there should be earthing of equipment and personnel and, unless incendive discharges can be ruled out, consideration should be given to explosion protection. For the same size container, if the MIE is $\leq 25\,mJ$ and there is a possibility of propagating brush discharges, there should be earthing of equipment and personnel and, unless incendive discharges can be ruled out, consideration should be given to explosion protection; in addition, earthed rods should be inserted into the container to assist relaxation of charge from the powder. If the non-metallic container is $> 5\,m^3$, for which the probability of incendive discharge from a dust cloud is as yet unknown, there should be earthing of equipment and personnel and, unless it can be shown that incendive discharges will occur neither from the bulk powder nor the dust cloud, consideration should be given to explosion protection; if there is a possibility of propagating brush discharges, consideration should be given to the use of earthed rods.

The Standard deals with the use of removable non-metallic liners in containers for solvent wet materials or dry powders. The effect of such a liner depends on whether it is used in a metal or in a non-conductive container. If the liner is used in a metal container, it may insulate the material being handled from earth via the metal and it may itself become charged, with the possibility of a propagating brush discharge. The standard strongly recommends that the liner be conductive with a surface resistivity not exceeding $10^{11}\,\Omega$. The precautions applicable to the equivalent unlined container should be taken. A liner with a higher resistivity should be used in a metal container only where this is essential, in which case expert advice is required. The precautions recommended by the standard for the case of a non-metallic liner in a non-conductive container are the same as those for a non-conductive container alone. The use of conductive liners in non-conductive containers is not recommended but, if practised, such liners should be earthed. In almost all

Table 16.40 *Some precautions against static electricity given in BS 5958: Part 2: 1991 – precautions for selected containments and equipment and operations involving liquids*

	Configuration/ operation	*Containment material*	*Precautions*
1.	Liquid storage tank	Metal	Vapour space reduction/atmosphere control Liquid conductivity Earthing of tank Avoidance of splash filling, fill pipe arrangements Liquid velocity Charge generators Relaxation time Gauging and sampling
2.	Liquid storage tank	Non-conductor	As (1) plus: limitation on use, earthing of liquid, hazardous areas
3.	Road/rail tanker	Metal	As (1) plus: hoses
		Non-conductor	As (2) plus: hoses
4.	Liquid/liquid and liquid/solid blending		Atmosphere control Earthing Agitator power
5.	Small containers for liquids	Metal	Earthing Liquid velocity
6.	Small containers for liquids	Non-conductor	As (5) plus: hazardous areas
7.	Ships and barges: loading		Atmosphere control Earthing Fill pipe Liquid velocity
8.	Ships and barges: tank cleaning		Atmosphere control Earthing

Table 16.41 *Some precautions against static electricity given in BS 5958: Part 2: 1991 – some limitations on liquid velocity for operations involving filling with liquids*

	Configuration/ operation	*Liquid conductivity* (pS/m)	*Liquid velocity*[a] (m/s)
1.	Liquid storage tank filling	≤ 50	≤ 7 General limit ≤ 1 Until fill pipe submerged ≤ 1 If immiscible phase present
		> 50	No limitation
2.	Road or rail tanker loading	≤ 50	Lower of (a) $u \leq 7$ (b) $ud \leq N$[b] ≤ 1 If immiscible phase present
3.	Small container filling	≤ 50	≤ 1 If immiscible phase present
		> 50	No limitation
4.	Ship or barge loading	≤ 50	≤ 1 Until fill pipe submerged ≤ 1 If immiscible phase present
		> 50	No limitation

[a] These are the liquid velocity limits given for metal containers.
[b] N is a constant with a value of $0.5\,m^2/s$ for liquid conductivities of $> 5\,pS/m$. The Standard states that the value to be applied for liquid conductivities of $\leq 5\,pS/m$ is a matter for debate and quotes values of 0.38 and $0.5\,m^2/s$ as having been accepted, but it also states that in the UK the value used is $0.5\,m^2/s$.

cases an essential precaution is that removal of the liner from the container, with the attendant risk of sparking, should be avoided in the presence of a flammable mixture.

Another type of container is the flexible intermediate bulk container (FIBC) used for powders. Typically, such containers are made of polypropylene fabric or some similar heavy duty material. Some have conducting thread woven into them. The variety of FIBCs, and the lack of data on their performance, are such that the standard gives only very general advice and recommends expert consultation. It does, however, state the basic principle that if an FIBC is made of a conducting material it should be earthed.

For liquid–liquid and liquid–solid blending, measures recommended in the Standard include atmosphere control, earthing of the container and limitation of agitator power.

The Standard also deals with a number of operations. One of these is gauging and sampling. Such operations are commonly carried out on storage tanks. The gauging and sampling equipment should be a made of a conducting material such as a metal or of wood or natural fibre. The resistivity of wood and natural fibre is such that they do not become highly charged or give incendive sparks. Use should not be made of metal chains or of synthetic polymers, which have high resistivity. All metallic parts on gauging and sampling equipment should be earthed, by connection to the earthed tank if it is a metal one or direct to earth if the tank is a non-conductive one. For liquids with conductivities of $\leq$50 pS/m, gauging and sampling operations should not be carried out during any charge generating operation, including filling, and after filling not until the lapse of a prescribed relaxation time. The relaxation times recommended are at least 30 minutes if the filling liquid has a separate water phase and a period of, say, 10 minutes if it does not. After any mixing operation the gauging and sampling should be deferred until the components have settled. After a cleaning operation that has generated a charged mist, gauging and sampling should be delayed until the mist has settled, which may take some hours. If the liquid conductivity is >50pS/m, gauging and sampling may be done at any time. Also, the foregoing restrictions on when gauging can be performed do not apply if it is done using fixed gauging equipment or through a fixed, earthed pipe extending to the bottom of the tank. Gauging and sampling should not be undertaken during adverse weather conditions such as thunderstorms or snow or hail storms.

Another operation considered is the manual addition of powders to flammable liquids. The flammable vapour should be contained within the receiving vessel, and dust cloud formation should be strictly controlled. The container being emptied should preferably be of metal or other conductive material and should be earthed. A paper sack can be earthed by contact with the earthed plant. Emptying from non-conductive containers is not generally recommended. The standard also gives precautions to be taken if there is a liner in the container being emptied, these precautions being similar to those described above in relation to the filling of lined containers. The receiving vessel and chutes should preferably be of metal or other conductive material and should be earthed. The Standard recommends against the use of non-conductive materials for such equipment. The risk of incendive discharge by the powder as it enters the receiver is assessed as generally low unless the chute is longer than 3 m or the powder has high resistivity, in which case expert advice is in order. For a liquid in the receiving vessel with a conductivity of >50 pS/m, it is sufficient to ensure that the liquid is earthed, either by contact with the earthed metal vessel or, if the vessel has a non-conductive lining, by a special earth point at the base of the receiver. If the liquid conductivity is $\leq$50 pS/m, and it cannot be reduced below this by a conductivity modifier, expert advice should be sought. An alternative basis of safety can be the elimination of a flammable atmosphere, but in this case it should be appreciated that air can enter with the powder. It may be necessary to monitor the oxygen content.

The Standard emphasizes that in operations generally, it should be ensured that the human body does not present an ignition risk.

The foregoing summary is no more than a sample from the detailed recommendations made in the Standard on a wide range of situations.

16.7.50 Precautions against static electricity: NFPA 77

In the USA the relevant standard is NFPA 77: 1988 *Static Electricity*. Its recommendations agree in broad outline with, but differ in some details from, those just described.

The precautions given for the handling of liquids include avoidance of entrained water and gas, avoidance of splash filling and gas bubbling, limitation of flow velocity, location of the fill pipe near the bottom of the container and provision of relaxation time.

The code gives detailed arrangements for a number of specific situations, including filling of storage tanks, road tankers, rail tank cars, small containers and drums.

Where bottom loading of road tankers is used, the code recommends limitation of the flow velocity or use of splash deflectors to prevent upward spraying.

It draws attention to the particular hazard of hydrogen containing small particles of oxide from the inside of containments. In this contaminated state the gas will generate charge. Its minimum ignition energy is very low.

16.7.51 Precautions against static electricity: Expert Commission

Another set of recommendations on static electricity are those of the Expert Commission for Safety in the Swiss Chemical Industry (1988). The following account summarizes some of the principal points.

The report gives guidance on a number of specific situations. For the handling of liquids, these include (1) liquid transfer through pipes and hoses, (2) liquid filling or emptying of small containers and drums under gravity, (3) liquid transfer by drum pumps, (4) liquid filling of agitated vessels, (5) operations at the open access port of an agitated vessel, (6) liquid filling of large glass vessels, (7) loading and unloading of road and rail tankers and (8) transfer and filtration of suspensions on filters and centrifuges close to the flashpoint.

Guidance is also given on the handling of powders. Separate consideration is given to the handling of

powders without and with flammable vapours. Specific situations considered include (1) 'open' charging of powder into flammable liquids, (2) discharging of solids containing flammable liquids from filtration apparatus, (3) charging and emptying of containers, (4) pneumatic conveying, (5) charging of powders into silos, (6) spray and fluidized bed drying and (7) ventilation, extraction and dust aspiration systems. For each situation the report rehearses the hazards and describes precautions. It gives a large number of diagrams showing in detail the configurations recommended.

For liquid transfer through pipes and hoses, the hazards are those already described. Precautions include exclusion of impurities such as water or dust, operation with the pipe full, limitation of the flow velocity and care with charge generators such as filters. Guidance is given on velocity limits for partially full pipes and for pipes conveying slurries of crystals, and on hose selection.

For liquid filling or emptying of small containers and drums under gravity, the hazards depend on whether the container is conductive or non-conductive, as described above. Precautions include taking the fill pipe close to the bottom of the container, and earthing of the container and fill pipe and of personnel. Liquids containing an immiscible component should be charged only into conducting containers. For liquids at a temperature less than 5°C below the flashpoint a table is given for the selection of a suitable type of container.

For liquid transfer by drum pumps, the hazards are charging of the liquid and sparking between the drum pump and the container. Precautions are to connect the drum pump both to the container being emptied and to that being charged and to earth it. The connectors should be permanently fixed to the drum pump so that it is clear that the connections need to be made. The connecting points should not be the openings of the drum or the container, as these are the very points where a flammable mixture is most likely to be present.

For liquid filling of agitated vessels, the situation particularly envisaged is the charging of a liquid using compressed air or inert gas, where the hazards are charging by turbulence and the creation of brush discharges between the liquid surface and internal fittings. Precautions include bottom filling or taking a top fill pipe close to the bottom, limitation of charging velocity, avoidance of discharging by 'blowing off' with air, and use of nitrogen blanketing. Guidance is also given on the alternative procedure of charging under vacuum and on special precautions for enamelled vessels.

For operations at the open access port of an agitated vessel, the hazard is sparking between the liquid surface of the reaction mass and an approaching metal object, or between the port flange and a conducting object in contact with the liquid. Precautions include avoidance of sampling through open ports or, if this cannot be avoided, the use of non-conductive sampling devices and the observance of a relaxation time.

For liquid filling of large glass vessels, the hazards are charging of the liquid and the vessel by turbulence and sparking between conductive items. Precautions include earthing of metal parts, limitation of flow velocity and inerting. Guidance is given on the alternative procedure of charging under vacuum.

For loading and unloading of road and rail tankers, the hazards are charging of the liquid, the vehicle and even the driver when leaving the cab, and sparking between conductive items. Precautions include a connection between the vehicle and the fixed tank at the terminal and the use of conductive hoses and footwear.

For the transfer and filtration of suspensions on filters and centrifuges at temperatures less than 5°C below the flashpoint, the hazard is charge generation during the filtration or centrifugation so that the filter cake or isolated conductors become charged, and sparking between these and conductive items. Precautions include earthing and inerting.

For powders, the report distinguishes between powders without and with flammable vapours. It takes the dividing line as 1% flammable solvent; powders with less than this can be considered as essentially solvent free. For solvent-free powders the hazard is charging of large metal parts and sparking from these. Precautions include the earthing of such parts. Provided the solvent-free status of the powder is assured, the construction material of containments such as drums or pipes is not restricted. Containers with plastic liners are acceptable.

For powders which are handled in the presence of a flammable vapour, are wet with flammable solvent or are charged into flammable solvent, the report gives the following guidance. The hazards include charging not only of metal parts but also of the powder and of sparking from metal parts. There is a particular hazard of brush discharges. A large proportion of incidents due to static electricity occur with such systems. Precautions include earthing and inerting. For powders containing flammable solvents only earthed containers should be used.

Powders containing flammable solvents should not be poured from non-conductive containers or bags or through non-conductive ducts into a charging vessel. Nor should powders be poured into a vessel containing a flammable solvent from non-conductive containers or non-conductive ducts.

For the open charging of powder into flammable liquids, three cases are distinguished: Case A, non-combustible or high MIE powders; Case B1, open charging of powders into precharged solvent; and Case B2, open charging of solvent-wet solids into an empty container. Guidance is given for each of these cases.

For discharging of solids containing flammable liquids from filtration apparatus, including centrifuges, the hazard is charging of the filter cake, filter cloth and metal parts and sparking to conductive items. In some cases dust formation has been observed with solvent contents up to 10%. Precautions include conductive filters, discharging using earthed chutes and containers, non-conductive shovels, local exhaust ventilation and inerting. Non-conductive filters should be withdrawn slowly.

For charging and emptying of containers with powders containing flammable liquids, the hazard is charging and sparking to a conductive item or brush discharges. Precautions include the use of earthed, metal containers and the avoidance of non-conductive containers or non-conductive linings.

For pneumatic conveying, the hazards are charging of the pipe and of the powder, charge accumulation in silos and sparking between metal parts. Precautions include the use of earthed, metal pipes. If plastic piping is used, the flanges should be plastic also or, if metal, earthed.

Before discharge into a silo, the charge on powder can be reduced by first passing the powder through an earthed, metal cyclone.

For the charging of powders into silos, the hazard is as described above. In principle, a large, charged dust cloud could be created and could discharge, though the report states that no such cases are known. Precautions include the avoidance of internal insulating coatings, the use of conducting paints and the exclusion of tramp metal.

For spray and fluidized bed drying, the hazard is charging of metal parts and of the powder, and sparking. The high speed movement and the very dry atmosphere are conducive to high charge generation. Precautions include earthing and inerting.

For ventilation, extraction and dust aspiration systems, the hazard is charging of dust deposits and sparking. Precautions are the use of earthed metal rather than plastic ducting, the avoidance of sections of plastic duct or, if this is unavoidable, the use of bridging connections across such sections.

16.8 Electrical Equipment

Electrical equipment is widely used in process plant and may be a source of ignition unless close control is exercised.

In the UK the relevant legislation is as follows. For the premises to which it applies, the Factories Act 1961, Section 31, deals with hazard from flammable and explosive materials, but the main statutory requirements governing electrical apparatus are those given in the Electricity at Work Regulations 1989, which apply to all places of work. Regulation 6, on adverse or hazardous environments, states that:

> Electrical equipment which may reasonably foreseeably be exposed to – (a) mechanical damage; (b) the effects of weather, natural hazards, temperature or pressure; (c) the effects of wet, dirty, dusty or corrosive conditions; or (d) any flammable or explosive substance, including dusts, vapours or gases, shall be of such construction or as necessary protected as to prevent, so far as is reasonably practicable, danger arising from such exposure.

In addition, the Highly Flammable Liquids and Liquefied Petroleum Gases Regulations 1972 state in Regulation 9.1: 'No means likely to ignite vapour from highly flammable liquids shall be present when a dangerous concentration of vapours from highly flammable liquids may be reasonably expected to be present.' In general, these regulations apply to premises where the Factories Act applies. A highly flammable liquid is one which has a flashpoint below 32°C and supports combustion under specified test conditions.

The Petroleum (Consolidation) Act 1928 is also relevant in cases where petroleum spirit and certain other materials are kept.

The use of electrical apparatus in flammable atmospheres is a topic in which there is active development of standards and codes of practice. In consequence, there is a continuously changing situation and a rather large number of codes, which may contain contradictory provisions.

Some important British Standards on electrical protection are given in Table 16.42.

The relations between these standards are as follows. BS 5345: 1977– gives the overall philosophy of the use of electrical apparatus in flammable atmospheres. It supersedes the older code BS CP 1003: 1964–, which is obsolescent and is retained only for use with existing plants. BS 5345: Part 1 covers general recommendations and Part 2 covers hazardous area classification.

The principles and specific methods of safeguarding are dealt with in BS 4683: 1971–, BS 5501: 1977– and BS 5345: Parts 3–8.

There are several other relevant UK codes. Of particular importance are the Institute of Petroleum (IP) *Area Classification Code for Petroleum Installations* (the IP *Area Classification Code*) (1990 MCSP Pt 15) and the *Electrical Safety Code* (1991 MCSP Pt 1). Another, older code is the ICI *Electrical Installations in Flammable Atmospheres Code* (the ICI *Electrical Installations Code*) (ICI/RoSPA 1972 IS/91).

US codes include NFPA 70: 1993 *National Electrical Code* and API RP 540: 1991 *Recommended Practice for Electrical Installations in Petroleum Processing Plants*.

The international standard in this field is the International Electrotechnical Commission (IEC) *Publication 79, Electrical Apparatus for Explosive Gas Atmospheres*.

Codes and standards for hazardous area classification, as distinct from safeguarding, are given in the next section.

Organizations in the UK which are engaged in work in this field include the Electrical Research Association (ERA) and the Electrical Equipment Certification Service (EECS).

16.8.1 Hazardous area classification

The basis for the control of electrical equipment to prevent its acting as a source of ignition is the classification of plant according to the degree of hazard. Originally this procedure was commonly termed the 'electrical area classification', but it is now known by the more comprehensive term hazardous area classification (HAC), or classification of hazardous locations (CHL).

The definitions originally used in the UK for area classification and given in BS CP 1003: 1964– are based on divisions:

Division 0	An area or enclosed space within which any flammable or explosive substance, whether gas, vapour or volatile liquid, is continuously present in a concentration within the lower and upper limits of flammability.
Division 1	An area within which any flammable or explosive substance, whether gas, vapour or volatile liquid, is processed, handled or stored, and where during normal operations an explosive or ignitable concentration is likely to occur in sufficient quantity to produce a hazard.
Division 2	An area within which any flammable or explosive substance, whether gas, vapour or volatile liquid, although processed or stored, is so well under control that the production (or release) of an explosive or ignitable concentration in sufficient quantity to constitute a hazard is only likely to occur under abnormal conditions.

Table 16.42 *Selected British Standards on electrical protection*

BS CP 1003: 1964–	Electrical apparatus and associated equipment for use in explosive atmospheres of gas or vapour other than mining applications (obsolescent)[a]	
	Part 1: 1964	Choice, installation and maintenance of flameproof equipment and intrinsically-safe equipment
	Part 2: 1966	Methods of meeting the explosion hazard other than by use of flameproof or intrinsically-safe equipment
	Part 3: 1967	Division 2 areas
BS 5345: 1977–	Code of practice for the selection, installation and maintenance of electrical apparatus for use in potentially explosive atmospheres (other than mining applications or explosive processing and manufacture)	
	Part 1: 1989	General recommendations
	Part 2: 1983	Classification of hazardous areas
	Part 3: 1979	Installation and maintenance requirements for electrical apparatus with type of protection 'd'. Flameproof enclosure
	Part 4: 1977	Installation and maintenance requirements for electrical apparatus with type of protection 'i'. Intrinsically safe electrical apparatus and systems
	Part 5: 1983	Installation and maintenance requirements for electrical apparatus protected by pressurization 'p' and by continuous dilution, and for pressurized rooms
	Part 6: 1978	Recommendations for type of protection 'e'. Increased safety
	Part 7: 1979	Installation and maintenance requirements for electrical apparatus with type of protection N
	Part 8: 1979	Installation and maintenance requirements for electrical apparatus with type of protection 's'. Special protection
BS 229: 1957	Specification. Flameproof enclosure of electrical apparatus (obsolescent)	
BS 4137: 1967	Guide to the selection of electrical equipment for use in Division 2 areas (obsolescent)	
BS 1259: 1958	Intrinsically safe electrical apparatus and circuits for use in explosive atmospheres (obsolescent)	
BS CP 1013: 1965	Earthing	
BS 4683: 1971–	Specification for electrical apparatus for explosive atmospheres	
	Part 1: 1971	Classification of maximum surface temperatures
	Part 2: 1971	The construction and testing of flameproof enclosures of electrical apparatus
	Part 3: 1972	Type of protection N (withdrawn)
	Part 4: 1973	Type of protection 'e' (obsolescent)
BS 5501: 1977	Electrical apparatus for potentially explosive atmospheres	
	Part 1: 1977	General requirements
	Part 2: 1977	Oil immersion 'o'
	Part 3: 1977	Pressurized apparatus 'p'
	Part 4: 1977	Powder filling 'q'
	Part 5: 1977	Flameproof enclosure 'd'
	Part 6: 1977	Increased safety 'e'
	Part 7: 1977	Intrinsic safety 'i'
	Part 8: 1988	Encapsulation 'm'
	Part 9: 1982	Specification for intrinsically safe electrical systems 'i'
BS 6941: 1988	Specification for electrical apparatus for explosive atmospheres with type of protection N	

[a] Obsolescent. Replaced by BS 5345:1977–, but retained temporarily as a reference guide for existing plants.
[b] Obsolescent.

These definitions have been replaced in BS 5501: Part 1: 1977 and BS 5345: Part 1: 1989 with the international definitions of the International Electrotechnical Commission (IEC) which are in terms of zones:

Zone 0	A zone in which an explosive gas–air mixture is continuously present or present for long periods.
Zone 1	A zone in which an explosive gas–air mixture is likely to occur in normal operation.
Zone 2	A zone in which an explosive gas–air mixture is not likely to occur in normal operation and if it occurs will only exist for a short time.
Non-hazardous	An area in which an explosive gas–air mixture is not expected to be present in quantities such as to require special precautions for the construction and use of electrical apparatus.

The IP *Area Classification Code* also makes use of the following fluid categories:

Fluid Category A	A flammable liquid that, on release, would vaporize rapidly and substantially.
Fluid Category B	A flammable liquid, not in Category A, but at a temperature sufficient for boiling to occur on release.
Fluid Category C	A flammable liquid, not in Categories A and B, but which can, on release, be at a temperature above its flashpoint, or form a flammable mist.
Fluid Category G	A flammable gas or vapour.

The code gives further guidance on assignment to Category A.

In the USA, NFPA 70: 1993 gives in Section 500 the following classification of hazardous locations:

Class I	in which the combustible material is a gas or vapour.
Class II	in which the combustible material is a dust.
Class III	in which the combustible material is a fibre or flying material.

Each class is divided into Division 1 and Division 2, the distinction between the two being based on the frequency with which the substance may be present in the atmosphere.

The classification of hazardous locations given in API RP 500: 1991 is essentially the same as that in NFPA 70, but with some change of wording:

Class I	A location in which flammable gases or vapours are, or may be, present in the air in quantities sufficient to produce explosive or ignitable mixtures
Class I, Division 1	A location (1) in which ignitable concentrations of flammable gases or vapours exist under normal operating conditions; (2) in which ignitable concentrations of such gases or vapours may exist frequently because of repair or maintenance operations or leakage; or (3) in which breakdown or faulty operation of equipment or processes might release ignitable concentrations of flammable gases or vapours, *and* might also cause simultaneous failure of electrical equipment that could become a source of ignition.
Class I, Division 2	A location (1) in which volatile flammable liquids or flammable gases are handled, processed or used, but in which the liquids, vapours or gases normally will be confined within closed containers or closed systems from which they escape only in case of accidental rupture or breakdown of such containers or systems, or in case of abnormal operation of equipment; (2) in which ignitable concentrations of gases and vapours normally are prevented by positive ventilation, and that might become ignitable through failure or abnormal operation of the ventilating equipment; or (3) that are adjacent to a Class I, Division 1 location (and not separated by a vapour-tight barrier), and to which ignitable concentrations of gases or vapours might occasionally be communicated unless such communication is prevented by adequate positive-pressure ventilation from a source of clean air, and effective safeguards against ventilation failure are provided.

NFPA 497M: 1991 gives a grouping of atmospheric mixtures. API RP 500 gives the following partial listing:

Group A	Atmospheres containing acetylene.
Group B	Atmospheres such as butadiene, ethylene oxide, propylene oxide, acrolein, or hydrogen (or gases or vapours equivalent in hazard to hydrogen, such as certain manufactured gases).
Group C	Atmospheres such as cyclopropane, ethyl ether, ethylene, hydrogen sulphide or gases or vapours of equivalent hazard.
Group D	Atmospheres such as acetone, alcohol, ammonia, benzene, benzol, butane, gasoline, hexane, lacquer solvent vapours, methane, naphtha, natural gas, propane or gases or vapours of equivalent hazard.

16.8.2 Safeguarding of equipment

There are a number of methods available for the safeguarding of electrical equipment so that it is suitable for use in a hazardous area, but it is a fundamental principle that electrical equipment should not be located in a hazardous area if it is practical to site it elsewhere.

The methods of safeguarding traditionally used in the UK are listed in the ICI *Electrical Installations Code* as:

(1) segregation;
(2) flameproof enclosures;
(3) intrinsically safe systems;
(4) approved apparatus and apparatus with type of protection 's';
(5) pressurizing and purging;
(6) apparatus with type of protection 'N';

(7) Division 2 approved apparatus;
(8) apparatus with type of protection 'e';
(9) non-sparking apparatus and totally enclosed apparatus;
(10) apparatus for use in dust risks.

The *Code* discusses these methods and their application.

Reference is made to normally sparking, non-sparking and totally enclosed apparatus. The ICI *Code* describes these as follows. Normally sparking apparatus is that which in normal operation produces sparks, arcs or surface temperatures capable of igniting the flammable atmosphere. Non-sparking apparatus is that which in normal operation does not produce such sources of ignition, although it may do so as a result of electrical or mechanical failure. It includes Division 2 approved apparatus and apparatus with type of protection N. Examples of non-sparking apparatus include cage motors and solenoid valves.

Totally enclosed apparatus is that contained in an enclosure which renders the risk of entry of a flammable atmosphere small. Total enclosure is applied to lamp fittings. It may also be applied to non-sparking apparatus as an additional safeguard. An example of the latter is a totally enclosed cage motor.

The principle of segregation is the use of a fire-resistant impermeable barrier to create a lower risk zone or non-hazardous area where electrical equipment suitable for a lower classification can be used. An example is the use of a non-sparking motor in a Zone 2 area to drive a pump in a Zone 1 area, the two machines being connected by a shaft which passes through a gas-tight gland in a wall separating the two zones.

The methods of protection given above are now supplemented by a number of newer methods.

The British Standards governing safeguarding of electrical apparatus are principally BS 4683: 1971–, BS 5501: 1977– and BS 5345: Part 1: 1989. BS 229: 1957 also applies, but is obsolescent.

The certification of equipment is performed by the Electrical Equipment Certification Service (EECS). This body is the successor to the former British Approvals Service for Electrical Equipment in Flammable Atmospheres (BASEEFA). Guidance on the system operated by the EECS is given in EECG2 *Electrical Equipment Certification Guide* (1992). The EECS inherited from BASEEFA a system of SFA standards. As far as concerns the 'types of protection' described below, this system is now essentially obsolete, although some limited use is made of SFA 3009 for special protection 's' and of SFA 3102 for intrinsic safety 'i'.

The overall procedure for selecting electrical apparatus for flammable atmospheres is described in BS 5345: Part 1: 1989. The selection is made by establishing the zone type in which the apparatus is to be used and then selecting the appropriate apparatus on the basis of:

(1) temperature classification;
(2) apparatus group;
(3) environmental conditions.

There is a maximum surface temperature of the equipment which should not be exceeded. This corresponds to the ignition temperature of the gases or vapours involved. The relation between the apparatus Class T and the maximum surface temperature is given in BS 5345: Part 1: 1989 as follows:

Class	*Maximum surface temperature* (°C)
T1	450
T2	300
T3	200
T4	135
T5	100
T6	85

Apparatus is grouped according to the properties of the gases or vapours involved. BS 5345: Part 1: 1989 divides apparatus into: Group I, apparatus for mines susceptible to firedamp; and Group II, apparatus for places with potentially explosive atmosphere, other than mines susceptible to firedamp. In the present context it is only Group II which is of interest. This is itself is divided into subgroups.

BS 5345: Part 1: 1989 lists the following relationships between representative gases and the group and subgroup classifications:

Representative gas	*BS 5501*[a]	*BS 4683*	*BS 229*	*BS 1259*
Methane	I[b]	I[b]	I	1
Propane	IIA	IIA	II	2c
Ethylene	IIB	IIB	II	2d
Hydrogen	IIC	IIC	IV	2e
Acetylene	IIC	Not allocated	IV	2f
Carbon disulphide	IIC	Not allocated	IV	2f

[a] Reference is to the then current edition of these standards.
[b] For underground mining applications.

For BS 229 the entries refer to the former gas groups and for BS 1259 to the former apparatus class.

BS 5345: Part 1: 1989 gives data on the flammability characteristics of the common industrial gases. Most gases and vapours are classified in BS 5345: Part 1 as Group IIA.

The allocation to apparatus subgroup in BS 5345: Part 1: 1989 is on the basis of the maximum experimental safe gap (MESG) and/or minimum igniting current (MIC).

These apparatus groups and subgroups and the method of allocation follow broadly that given in BS 5501: Part 1: 1977. For flameproof enclosures the criterion is the MESG, which is related to the subdivision as follows:

	MESG (mm)
Subdivision A	> 0.9
Subdivision B	0.5–0.9
Subdivision C	< 0.5

The MESG was described in Section 16.2. For intrinsically safe apparatus the criterion is the MIC ratio, which is related to the subdivision as follows:

	MIC
Subdivision A	> 0.8
Subdivision B	0.45–0.8
Subdivision C	< 0.45

The MIC is the ratio of the minimum igniting current for the gas or vapour to that for laboratory methane. A gas or vapour is assigned to a subdivision on the basis either of its MESG, of its MIC ratio, or both.

The methods of safeguarding recognized in BS 5345: Part 1: 1989 are shown in Table 16.43, which gives the definitions for each type of protection and cross-references to other standards. Similar, but in some cases not identical definitions, are given in BS 4683: 1971– and BS 5501: 1977.

Type of protection 'd' is a flameproof enclosure. The principle of a flameproof enclosure is that a flammation or explosion may occur in the enclosure, but a flame does not then travel back through any opening. There are maximum permissible dimensions for an opening in a flameproof enclosure. The opening needs to be of sufficient length and construction to prevent the passage of flame. MESGs were discussed in Section 16.2. The equipment should be sufficiently robust to withstand an occasional explosion without distorting, otherwise the dimensions of the gap may increase above the safe level. Alteration of the internals of a flameproof enclosure is not allowed because of the possible hazard of pressure piling.

Where a flameproof enclosure is exposed to wet weather it should be weatherproof. Weatherproofing is normally effected by the use of gasketed joints additional to and separate from the flame paths. For other apparatus suitable grease or tape is usually used. Protection against corrosion is also necessary in some applications.

Flameproof enclosures are classified by T Class and by apparatus subgroup. The main example of flameproof enclosures is the casing of flameproof electric motors.

Type of protection 'i' is intrinsically safe apparatus or system. The principle of intrinsic safety is that there is insufficient energy in the system to given incendive sparking or heating effects.

Two categories of intrinsically safe system are recognized in BS 5345: Part 4: 1977– ia, suitable for use in hazardous areas including Zone 0; and ib, suitable for use in hazardous areas excluding Zone 0.

In an intrinsically safe system it is necessary to take precautions to ensure that the power source of the system cannot release unsafe amounts of energy in the hazardous area and also that power from other sources cannot invade the system. There are thus requirements for insulation, earthing, screening, etc.

There are two main types of intrinsically safe system. One has some parts in the hazardous area, but the power supply is in the non-hazardous area. With this method it is necessary not only that the equipments in both areas be intrinsically safe but also that they be matched so that the system also is intrinsically safe. The power supply should be such as not to overload the current-limiting devices. Where the power supply is from the mains, it is usually necessary to use an inviolate transformer. Current limitation is then effected by inviolate resistors. Alternatively, barrier units may be used to limit both voltage and current.

The other system has all parts in the hazardous area and has its own power supply such as a battery. This type of system may be a fixed installation or a portable apparatus. In the former case it should again be intrinsically safe as a system.

It is particularly important with an intrinsically safe system that the system is not used outside the scope of the certification. Intrinsically safe systems are classified by T Class and by apparatus subgroup.

Since the minimum ignition energy of flammable mixtures is very small, this method of safeguarding is applicable only to low power systems, in particular instrumentation. Examples of intrinsically safe systems include instrument systems and portable gas detectors. Further information is given in *Intrinsic Safety* by Redding (1971a).

Type of protection 'p' is pressurization, continuous dilution and purging. Pressurizing and purging are used to control the atmosphere in a room or apparatus. Such control allows the safe use of electrical apparatus which otherwise would be hazardous.

In pressurizing, a positive pressure of air or inert gas is maintained in the enclosure so that the flammable material cannot enter. In purging, a flow of air or inert gas is maintained through the enclosure so that a flammable atmosphere does not form. Sometimes a combination of pressurization and purging may be employed.

Mechanical ventilation may be used for pressurization and purging. In the latter case the ventilation may be a forced or induced draught. Alternatively, an air or gas supply may be used.

Air is a suitable pressurizing medium and is generally preferable to inert gas, because it does not constitute an asphyxiation hazard. For purging, inert gas provides a higher degree of protection against flammability hazard and is suitable for small enclosures, but air is preferable for large enclosures and rooms on account of the asphyxiation hazard. The source of air or inert gas should be free of flammables and should be reliable. It may be necessary to clean and/or dry the air or inert gas.

It is recommended in BS 5501: Part 3: 1977 that the minimum overpressure in a pressurized enclosure should be 0.5 mbar.

The ICI *Code* states that pressurizing is not suitable for Zone 0. For Zone 1 with normally sparking apparatus there should be a pressure failure interlock and alarm. The interlock should disconnect the electrical supply on failure of pressure, except where this could create a hazardous condition, in which case other precautions are necessary. For Zone 1 with non-sparking apparatus and for Zone 2 with normally sparking apparatus there should be a pressure alarm. The action to be taken on failure of purging requires consideration of the particular circumstances.

Further details of pressurizing and purging, including monitoring systems, room and enclosure design, piping and ducting design and auxiliary apparatus are given in BS 5345: Part 5: 1983 and in the ICI *Code*.

Table 16.43 *Types of electrical protection in BS 5345: 1989 (Reproduced by permission of the British Standards Institution)*

Type of protection	*Title*	*Description*
d	Flameproof enclosure	A method of protection where the enclosure for electrical apparatus will withstand an internal explosion of the flammable gas or vapour (for which it is designed) that may enter it, without suffering damage and without communicating the internal flammation to the explosive atmosphere for which it is designed, through any joints or structural openings in the enclosure
i	Intrinsically safe apparatus or system	A protection technique based upon the restriction of electrical energy within apparatus and in the interconnecting wiring, exposed to a potentially explosive atmosphere, to a level below that which can cause ignition by either sparking or heating effects. Because of the method by which intrinsic safety is achieved it is necessary that not only the electrical apparatus exposed to the potentially explosive atmosphere, but also other (associated) electrical apparatus with which it is interconnected, is suitably constructed.
p	Pressurization, continuous dilution and pressurized rooms	A method of protection using the pressure of a protective gas to prevent the ingress of an explosive atmosphere to a space that may contain a source of ignition and, where necessary, using continuous dilution of an atmosphere within a space that contains a source of emission of gas, which may form an explosive atmosphere
e	Increased safety	A method of protection by which additional measures are applied to an electrical apparatus to give increased security against the possibility of excessive temperatures and of the occurrence of arcs and sparks during the service life of the apparatus. It applies only to an electrical apparatus, no parts of which produce sparks or arcs or exceed the limiting temperature[a] in normal service
N	Type of protection N	A type of protection applied to an electrical apparatus such that, in normal operation, it is not capable of igniting a surrounding explosive atmosphere, and a fault capable of causing ignition is not likely to occur
s	Special protection	A concept for those types of electrical apparatus that, by their nature, do not comply with the constructional or other requirements specified for apparatus with established types of protection, but that nevertheless can be shown, where necessary by test, to be suitable for use in hazardous areas in prescribed zones
o	Oil immersion	A method of protection where electrical apparatus is made safe by oil immersion in the sense that an explosive atmosphere above the oil or outside the enclosure will not be ignited
q	Powder/sand filling	A method of protection where the enclosure of electrical apparatus is filled with a mass of granular material such that, if an arc occurs, the arc will not be liable to ignite the outer flammable atmosphere
m	Encapsulation	A type of protection in which parts that could ignite an explosive atmosphere by either sparking or heating are enclosed in a compound in such a way that this explosive atmosphere cannot be ignited

[a] Limiting temperature is defined in BS 5345: Part 6: 1976.

Examples of enclosures which may be pressurized with air or inert gas are a totally enclosed motor and an instrument cubicle. Also a control room is often fitted with double doors, forming an air lock, and pressurized with air. Examples of enclosures which may be purged or pressurized/purged are rooms or instrument cubicles containing instruments analysing flammable gas.

Type of protection N is defined in terms of the degree of protection achieved rather than of the particular means by which this is done. The general characteristics of such apparatus are that under normal operation it does not produce an arc or spark except where the latter occurs in an enclosed break device, has insufficient energy to cause ignition of a flammable atmosphere or

occurs in a hermetically sealed device and does not develop a surface temperature capable of igniting a flammable atmosphere.

Apparatus with type of protection N complies with another British Standard which specifies this type of protection, e.g. BS 5000: Part 16: 1985 for motors.

Guidance on the construction and testing for type of protection N is given in BS 6981: 1988.

Before the introduction of type of protection N, apparatus could be submitted to HM Factories Inspectorate (HMFI) for approval for use in Division 2 applications, the basis of examination being BS 4137: 1967 *Guide to the Selection of Electrical Equipment for Use in Division 2 Areas*. If an apparatus was considered suitable for use in a Division 2 area, HMFI issued a letter to this effect and the apparatus was then commonly referred to as 'Division 2 approved'.

Type of protection 'e' is again defined in terms of the degree of protection achieved. It has features in common with type of protection N, but is more stringent. Apparatus with type of protection 'e' complies with BS 5501: Part 6: 1977.

Special protection 's' deals with 'approved' apparatus. This is equipment for which there is no specific British Standard. It is covered instead by the approval system.

'Approved' apparatus is that which has been approved for use in flammable atmospheres by HMFI. This approval system operated up to 1969, the list of approved equipment being given in HMSO *Form F931 Intrinsically Safe and 'Approved' Electrical Apparatus*. This was subsequently superseded by certification as special protection 's' in accordance first with BASEEFA *Certification Standard SFA 3009* and then with the EECS certification system. Apparatus with type of protection 's' is classified by T Class and by apparatus subgroup. Examples of approved equipment include compressed air-driven generator and lamp sets, and battery handlamps.

Before the introduction of 'Division 2 approved' apparatus and apparatus with type of protection N, use was made in Division 2 areas of non-sparking apparatus and of totally enclosed apparatus.

There are three other types of protection recognized in BS 5345: Part 1: 1989. These are oil immersion 'o', powder/sand filling 'q' and encapsulation 'm'. Compounds used for encapsulation include thermosetting, thermoplastic and elastomeric compounds.

There is much less guidance on dust risks, but some is given in the ICI *Code*. For dusts the most widely used method of safeguarding is a combination of (1) enclosure of apparatus and (2) elimination of hot surfaces.

The apparatus is enclosed so as to limit the amount of dust which can come in contact with sources of ignition and it is designed so that in normal operation its surface temperature does not exceed the ignition temperature of the dust in cloud or layer form. Other methods which may be used with dust risks include segregation, intrinsically safe systems and pressurizing or purging.

There are certain general precautions which should be taken with all the methods of safeguarding described. Apparatus should be used only for the purpose for which it has been designed and certified. It should not be altered by modification. It should not be allowed to deteriorate due to weather or corrosion. It should be properly maintained.

Table 16.44 *Selection of methods of safeguarding electric apparatus in hazardous areas in BS 5345: 1989 (Reproduced by permission of the British Standards Institution)*

Zone	*Type of protection*	*Part of* BS 5345
0	'ia' Intrinsically safe apparatus or system	4
	's' Special protection (specifically certified for use in Zone 0)	8
1	Any explosion protection suitable for Zone 0 and:	
	'd' Flammable enclosure	3
	'ib' Intrinsically safe apparatus or system	4
	'p' Pressurization, continuous dilution and pressurized rooms	5
	'e' Increased safety	6
	's' Special protection	8
2	Any explosion protection suitable for Zones 0 or 1 and:	
	N[a] Type of protection N[b]	7
	'o' Oil-immersion	9[c]
	'q' Sand filling[d]	9[c]

[a] Alternatively, apparatus that in normal operation is not capable of producing ignition capable arcs, sparks or surface temperatures may also be acceptable for use in Zone 2 where it has been assessed by persons who should:
(a) be familiar with the requirements of any relevant standards and codes of practice and their current interpretations;
(b) have access to all information necessary to carry out the assessment;
(c) where necessary, utilize similar test apparatus and test procedures to those used by recognized testing stations.

[b] Whereas in BS 6941 the type of protection is known as type N, in IEC publication 79-15 it is designated type 'n';

[c] In preparation.

[d] The use of apparatus with type of protection 'q' in Zone 1 is under consideration.

BS 5345: Part 1: 1989 gives a scheme for the selection of apparatus and systems, as shown in Table 16.44. Intrinsic safety is applied in all zones, but the type used should be suitable for the zone. The same applies to special protection 's'. The principal application of flameproof enclosures is in Zone 1. Pressurization and purging is applicable in Zones 1 and 2. Of the methods involving enhanced safety, type of protection 'e' is suitable for Zones 1 and 2, whilst type of protection N is suitable for Zone 2.

Other aspects of electrical systems in flammable atmospheres include: the installation of electrical equipment, particularly cabling; the inspection and maintenance of equipment; and electronic instrumentation. These are treated in detail in BS 4683: 1971–, BS 5501: 1977 and the ICI *Code*.

16.8.3 Electrical surface heating

The methods of safeguarding described above have been developed primarily for equipment such as electric motors and electronic instruments in which heating is undesirable. Their application to apparatus the prime purpose of which is heating requires separate treatment.

Electrical surface heating (ESH) is widely used in process plants and constitutes another potential source of ignition.

Types of heater used include (1) flexible heaters (fabric, braid, mesh), (2) heating cable, (3) panel heaters and (4) parallel circuitry heaters. The latter are often purpose made and may be in panel, mantle or jacket form.

An account of the design of electrical surface heaters for use in hazardous areas has been given by Dobie, Cunningham and Reid (1976). Their approach to safeguarding is to design the apparatus so that for a given workpiece surface temperature (e.g. pipe temperature) the maximum linear power loading (W/m) cannot give an element surface temperature in excess of the ignition temperature of the flammable atmospheres as given in BS 4683: Part 1: 1971. The equipment is also designed so as not to give rise to hazards from arcs and sparks.

Guidance on EHS devices, including their use in hazardous areas, is given in BS 6351 *Electrical Surface Heating*, of which Part 1: 1983 deals with specification, Part 2: 1983 deals with design and Part 3: 1983 deals with installation, testing and maintenance. Part 1 requires that an ESH device for use in a hazardous area should *inter alia*: (1) comply with type of protection 'e', N, 'd', 's', 'm' or 'p'; (2) be assigned a temperature classification; (3) be given a type test to establish the maximum surface temperature; and (4) comply with respect to the terminations and markings with specified in British Standards. Procedures are given for type testing, a distinction being made between ESH devices which have self-limiting characteristics and those which do not.

BS 6351: Part 2: 1983 sets certain minimum safety requirements for all ESH devices. It gives a system of service categories with a two-digit code, the first digit indicating the probability of the presence of water and the second the risk of mechanical damage. 0 denotes no risk, 1 low risk and 2 high risk: thus, for example, a coding of 00 denotes no risk in both categories and one of 22 high risk in both categories. The principal requirements referred to are (1) overcurrent protection, (2) residual current protection with trip indication, (3) means of isolation and (4) overtemperature limitation. Overcurrent protection and means of isolation are required for all ESH devices. For types of protection N and 'e' all four requirements apply.

Part 3 states isolation and permit-to-work requirements.

Further recommendations for ESH are given in the ICI *Electrical Installations Code.*

16.9 Hazardous Area Classification

The exclusion of sources of ignition is effected on process plant by a system of hazardous area classification (HAC). The principles of hazardous area classification have been outlined in Chapter 10 in relation to plant layout. In this section consideration is given to the application of these principles.

Hazardous area classification is the subject of a number of codes and standards. These include BS 5345 *Code of Practice for the Selection, Installation and Maintenance of Apparatus for Use in Potentially Explosive Atmospheres (Other than Mining Applications or Explosive Processing and Manufacture)*, including Part 1: 1989 *General Recommendations* and, in particular, Part 2: 1983 (1990) *Classification of Hazardous Areas*. Other relevant British Standards have been given in Section 16.8. Influential codes have been those of the successive IP codes and the ICI *Electrical Installations in Flammable Atmospheres Code* (the ICI *Electrical Installations Code*) (ICI/RoSPA 1972 IS/91). The current IP code is *Area Classification Code for Petroleum Installations* (the IP *Area Classification Code*) (1990 MCSP 15).

In the USA, NFPA codes include NFPA 70: 1993 *National Electrical Code*, NFPA 497A: 1992 *Classification of Class I Hazardous Locations for Electrical Installations in Chemical Plants*, NFPA 497B: 1991 *Recommended Practice for the Classification of Class II Hazardous (Classified) Locations for Electrical Installations in Chemical Plants* and NFPA 497M: 1991 *Classification of Gases, Vapors and Dusts for Electrical Equipment in Hazardous (Classified) Locations*. API RP 500: 1991 *Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Facilities* consolidates previous separate codes (RP 500A, 500B and 500C).

Other accounts of hazardous area classification include *Classification of Hazardous Locations* (A.W. Cox, Lees and Ang, 1990) and those by Swann (1957, 1959), Levine (1965a,b, 1968a,b, 1972a, 1983), Magison (1966, 1975, 1978), Burgoyne (1967b, 1969, 1971), Bartels (1971a, 1975a,c, 1977–), O'Shea (1982), Palles-Clark (1982), Peck and Palles-Clark (1982), Fordham Cooper (1986) and Mecklenburgh (1986).

Electrical safety and hazardous area classification has been the subject of a series of symposia by the IEE (1971, 1975, 1982, 1988 Conf. Publs 74, 134, 218 and 296, respectively; 1982 Coll. Dig 82/26).

Traditionally, hazardous area classification has centred around electrical equipment and has been the province of electrical engineers. Electric motors, instruments and other electrical equipment have to be present on plant, but may constitute potential sources of ignition. It is necessary, therefore, to assess the ignition risk and to match the equipment to it. This has been done by a system of area classification.

As already described, however, there are many other potential ignition sources on plant and a more balanced approach is called for. The modern approach to hazardous area classification involves the control of all sources of ignition and deals not only with design but also with activities such as operation and maintenance. There is a tendency for chemical engineers to be much more involved.

16.9.1 Hazardous area classification systems

The hazardous area classification system currently applicable in the UK is that of the IEC and is outlined in Chapter 10 and in Section 16.8 where accounts are given of the system of zones used (Zone 0, Zone 1 and Zone 2) together with definitions of these zones.

In the USA, two principal systems are those of the National Fire Protection Association (NFPA) and the American Petroleum Institute (API) which are also described in Section 16.8.

16.9.2 ICI *Electrical Installations Code*

The ICI *Electrical Installations in Flammable Atmospheres Code* (the ICI *Electrical Installations Code*) (ICI/RoSPA 1972 IS/91) describes the two basic methods of hazardous area classification: (1) the generalized method

and (2) the source of hazard method. It remains a principal guide for the latter. Classification of electrical areas is not an exact science and inevitably involves a degree of judgement. There are, however, a number of guidelines available.

The terms 'normal' and 'abnormal' require some interpretation. Normal conditions should be taken to be not ideal but real conditions as they actually exist, taking into account the precautions which are taken on a well run plant. Abnormal conditions should be read to refer not to catastrophic accidents such as a major equipment rupture but to events which are generally non-catastrophic such as a pump gland or pipe gasket failure.

The stages of the classification process are (1) identification of the hazard, (2) assessment of the hazard, and (3) delineation of the zone. The classification should be comprehensive. An area where flammable materials are not to be handled is non-hazardous, but this status should be formally established.

A basic distinction is between (1) well ventilated locations and (2) poorly ventilated locations. Ventilation is here interpreted in a broad sense and covers the whole question of the dispersion of vapours and liquids from leaks and spillages. Thus it is necessary to consider how much flammable material may escape, whether an escape is continuous or not, whether it is lighter or heavier than air, whether there may be jet effects, whether the liquid may travel outside the area on the surface of water on the ground or in drains or pipe trenches, and what the influence of the plant topography is.

There are two basic approaches to area classification. These are (1) the generalized method and (2) the source of hazard method. The generalized method is the older and involves making a judgment on the appropriate classification for a fairly large area of plant.

The ICI *Code* gives guidance for both the generalized and source of hazard methods. For the former a Zone 0 classification is necessary for locations such as vapour spaces in closed storage tanks or closed process vessels in which a flammable atmosphere may exist continuously or for long periods and immediately above an open tank or vessel containing a flammable liquid. Locations where in normal operation there may be release of flammable materials sufficient to cause a hazard either from relief valves or vents designed to make such release or from other sources such as vessels, pumps or pipes, should be classified as Zone 1. Classification as Zone 2 is acceptable provided that there are no releases in normal operation of flammable materials sufficient to cause a hazard, that relief valves and vents release flammable materials only under abnormal conditions and that the area is well drained and ventilated so that any abnormal occurrence of a flammable atmosphere is rapidly dispersed.

The *Code* states that it is characteristic of the generalized method that it gives a large Zone 1. The typical pattern is as follows. An area somewhat larger than that occupied by the process equipment is classified as either Zone 1 or Zone 2. If it is Zone 1, it may or may not be surrounded by a Zone 2. There may be isolated Zones 0 within a Zone 1 or a Zone 2.

While this blanket application of a Zone 1 classification is in itself conservative, it is also expensive, and there may be a tendency, which should be guarded against, to ignore a few high hazard points and classify as Zone 2 an area which should be Zone 1.

The source of hazard method is the newer approach and involves identifying, assessing and delineating affected areas for individual sources of hazard. The latter are classified according to the expected frequency and period of release of flammable materials. The classification together with the suggested quantitative guidelines is as tabulated below:

Source of hazard	*Period of release*	*Frequency* (hazards/year)
0 (Continuous)	Long periods	>1000
1 (Primary)	Frequent or if infrequent persistent	10–1000
2 (Secondary)	Infrequent and of short duration	<10

The characteristic area classification yielded by the source of hazard method is predominantly Zone 2 with small isolated Zones 1. Zones 0 may also occur in either Zones 1 or Zones 2.

In a well ventilated situation the extent of the zone is determined essentially in both methods by the distance at which it is judged that the flammable atmosphere will fall below its lower flammability limit.

In a poorly ventilated situation it is necessary to pay particular attention to the following aspects:

(1) sources of hazard which are continuous should be avoided or provided with special ventilation;
(2) each room in a building should be given separate consideration for possible sources of hazard;
(3) mobile sources of hazard should be taken into account;
(4) spillage hazards associated with portable or transportable vessels or open handling of liquids should be taken into account.

For a room which does not contain a source of hazard the classification depends on the probability of flammable materials entering the room and on the ventilation and may be Zone 1, Zone 2 or non-hazardous. In general, mechanical ventilation may be used as a means of modifying the classification for an enclosed space.

The extent of a zone in a poorly ventilated situation is again determined for both methods essentially by the dilution of the flammable atmosphere below its flammability limit. In confined situations, however, even the source of hazard method tends frequently to lead to Zone 1 classifications, so that there is less difference between the two methods in this case.

Some area classifications are illustrated in Figures 16.63 and 16.64. Figure 16.63(a) shows a classification for a reciprocating or centrifugal compressor handling a gas lighter than air (e.g. hydrogen or fuel gas) in a building with open sides and ventilation. There is a Zone 1 around the compressor. For a reciprocating compressor this Zone 1 is a sphere of 0.5 m radius all round the gland, cylinder, and frequently operated drain points or vents, and for a centrifugal compressor it is a sphere of 0.5 m radius all round the seal and a sphere of 1 m

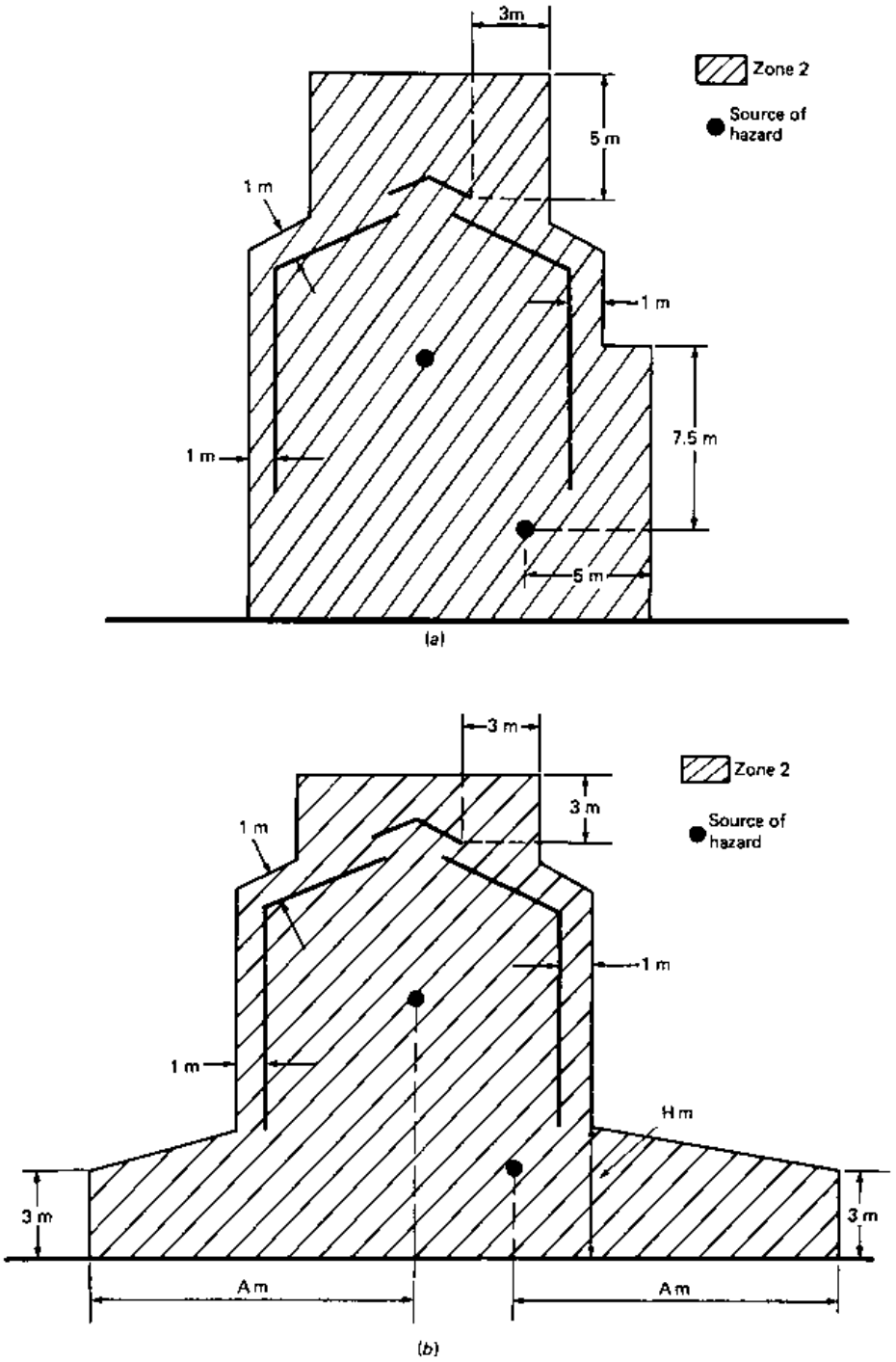


Figure 16.63 *Hazardous area classification – ICI Electrical Installations Code (Imperial Chemical Industries Ltd, ICI/RoSPA 1972 IS/91; reproduced with permission): zoning for a reciprocating or centrifugal compressor handling flammable gas in building with open sides and roof ventilation: (a) compressor handling a lighter than air gas; (b) compressor handling a heavier than air gas. Extent of Zone 2: for gases heavier than air, up to 30 bar, up to 100°C (e.g. ethylene and propylene refrigerants), A is 15 m; for supercritical ethylene, up to 100 bar, A is 30 m; dimension H is 3 m or height of the wall opening, whichever is the greater*

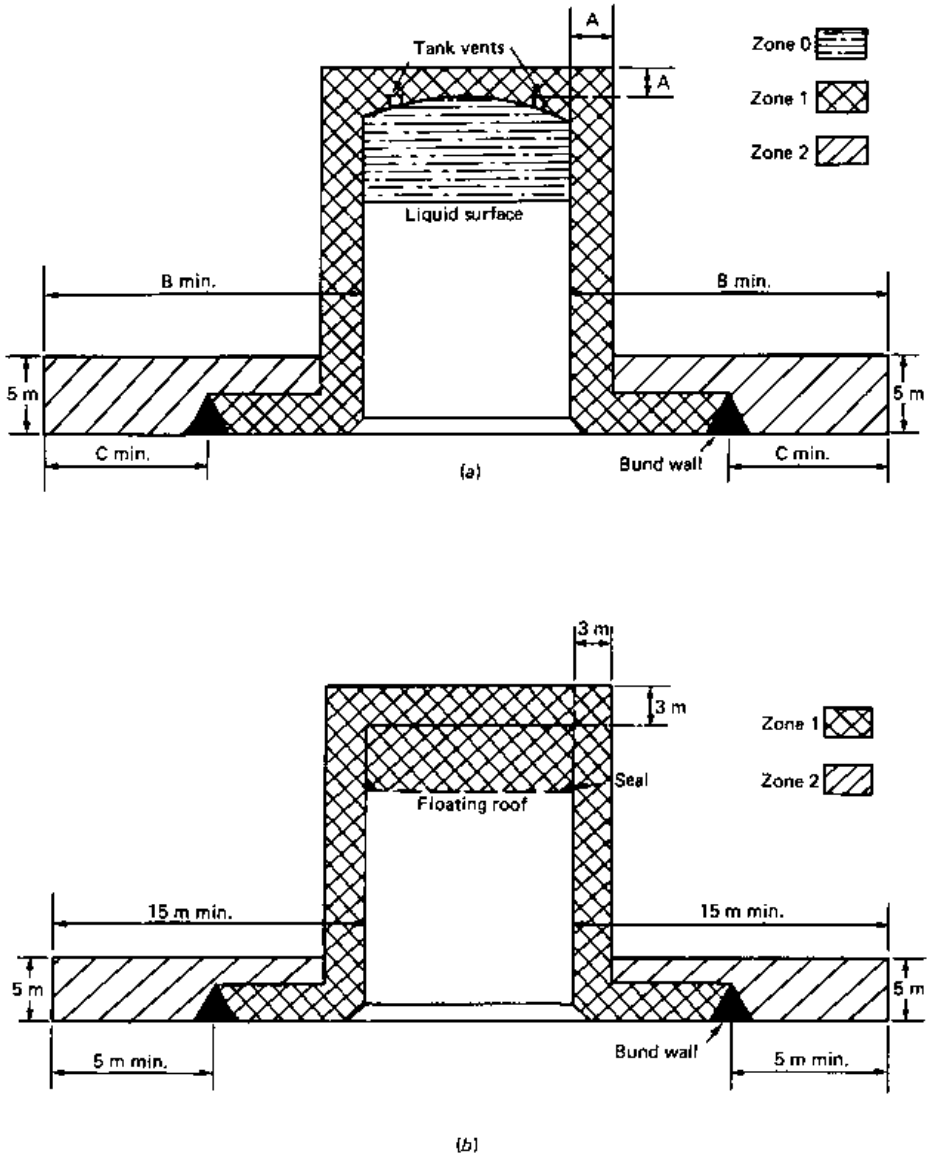


Figure 16.64 *Hazardous area classification – ICI Electrical Installations Code (Imperial Chemical Industries Ltd, ICI/RoSPA 1972 IS/91; reproduced with permission): zoning for a storage tank holding a flammable liquid with flash point below 32°C: (a) fixed roof tank; (b) floating roof tank. Extent of Zones I and 2: for a tank with capacity greater than 50 m³, A is 3 m and for a tank with smaller capacity A is 1.5 m; Zone 2 extends B m minimum from the tank side and C m minimum from the bund. For a tank with capacity greater than 100 m³ B and C are 15 and 5 m respectively; for a tank with a capacity between 50 m³ and 100 m³, B and C are 6 and 2.5 m, respectively; while for a tank with capacity below 50 m³ smaller distances may be appropriate*

radius around the seal-oil tank cover and vent and around seal–oil traps. Figure 16.63(b) shows a classification for a reciprocating or centrifugal compressor handling a gas that is heavier than air (e.g. ethylene or propylene refrigerants). The Zones 1 are the same as for the previous case.

Figures 16.64(a) and 16.64(b) show, respectively, classifications for a fixed roof and a floating roof storage tank for a flammable liquid with a flashpoint below 32°C.

The ICI *Code* also deals with area classification for flammable dusts. The basic principles of classification are similar to those for flammable gases and liquids, but it is

recognized that the behaviour of dusts is generally rather less predictable.

The definition of the zones in the ICI *Code* includes dusts and has already been given. In this case the source of hazard method is less useful and the generalized method is usually more appropriate.

Since dust presents a hazard in layer as well as in cloud form, it is necessary, irrespective of the area classification, to ensure that any surface on which dust can settle is below the ignition temperature of the dust in layer form. In exceptional cases where a surface temperature higher than the ignition temperature of the dust is required for process reasons, the equipment should be designed and operated so as to prevent the accumulation of dust on its surface and the formation of dust clouds.

16.9.3 IP *Area Classification Code*

The IP *Area Classification Code for Petroleum Installations* (the IP *Area Classification Code*) (1990 MCSP Pt 15) is written for petroleum installations, but the principles are of wider applicability. The code utilizes the IP classification of fluids given in Chapter 10 and the British Standard classification of hazardous locations and IP grouping of atmospheric mixtures given in Section 16.8. The principal contents of the code are listed in Table 16.45 and its application is shown in Figure 16.65.

The code emphasizes that hazardous area classification is not intended to deal with catastrophic events, but with more commonly occurring releases. In the design of new plant, or in plant modification, hazardous area classification should be carried out before the design and layout are finalized, and reviewed again on completion of the design.

The code describes two methods of hazardous area classification: (1) the method of direct example and (2) the point source method.

Information required

The information required for the conduct of hazardous area classification includes (1) the classification of the fluid(s), (2) the flow diagram, (3) the piping and instrument diagram, (4) the plant layout, (5) the equipment features, including operation and (6) the ventilation.

Table 16.45 *Principal contents of the IP Area Classification Code (IP, 1990 MCSP Pt 15)*

1. Introduction
2. The technique of hazardous area classification
3. The classification of storage tankage, bulk loading and unloading by road and rail, petroleum jetties, and bulk distribution and marketing facilities by the method of direct example
4. The classification of drilling rigs and other equipment systems used in well operations and production wellhead areas
5. Alternative procedure for classification of an upstream or downstream petroleum sector facility by consideration of the individual point source
6. Variation in ventilation conditions
7. Application to the selection and location of electrical facilities
8. Application to the control and location of ignition sources other than electrical

Classification of petroleum fluids

Petroleum fluids are classified by flashpoint. The code gives in Appendix A details of the IP classification by flashpoint. This classification system is described in Chapter 10. Fluids are classed as Class 0 (LPG); Class I; Class II(1) or II(2); Class III(1) or III(2); and Unclassified.

A further, supplementary classification by fluid category, utilized in the point source method, is given in the code in Appendix B. This categorization has been described in Section 16.8.

General approach

The general approach, described in the Chapters 1 and 2 of the IP *Code*, is to identify the sources and grades of release, and then to assign the appropriate zones. The grades of release are defined as:

Continuous grade release	A release that is continuous or nearly so, or that occurs for short periods which occur frequently
Primary grade release	A release that is likely to occur periodically or occasionally in normal operation
Secondary grade release	A release that is unlikely to occur in normal operation and, in any event, will do so only infrequently and for short periods

The grade of release reflects the frequency and duration of the release.

The *Code* gives the following rule of thumb to assist in the assignment of the grade of release. A release should be treated as continuous if it is likely to be present for more than 1000 h/year, as primary if present for more than 10 but less than 1000 h/year and as secondary if present for less than 10 h/year.

For open air conditions, there is a direct relation between the grade of release and the type of zone to which it gives rise, the continuous grade corresponding to Zone 0, the primary grade to Zone 1 and the secondary grade to Zone 2. However, this relationship applies only where the ventilation corresponds to unre stricted open locations with good natural ventilation. Poor ventilation may require the use of a more stringent zone, whilst very good ventilation may allow a relaxation to a less stringent one. There are certain guiding principles which govern hazardous area classification.

Where a number of fluids are handled, as in storage and loading/unloading facilities, the classification should be based on the most volatile.

The identification of sources of continuous and primary grade releases, and the delineation of Zones 0 and 1, should be as complete as possible. Many plant areas are designated as Zone 2. Particular attention should be given to sources of secondary grade releases at the edge of the plant, since these will tend to define the extent of the Zone 2. In some cases it is not practical to determine

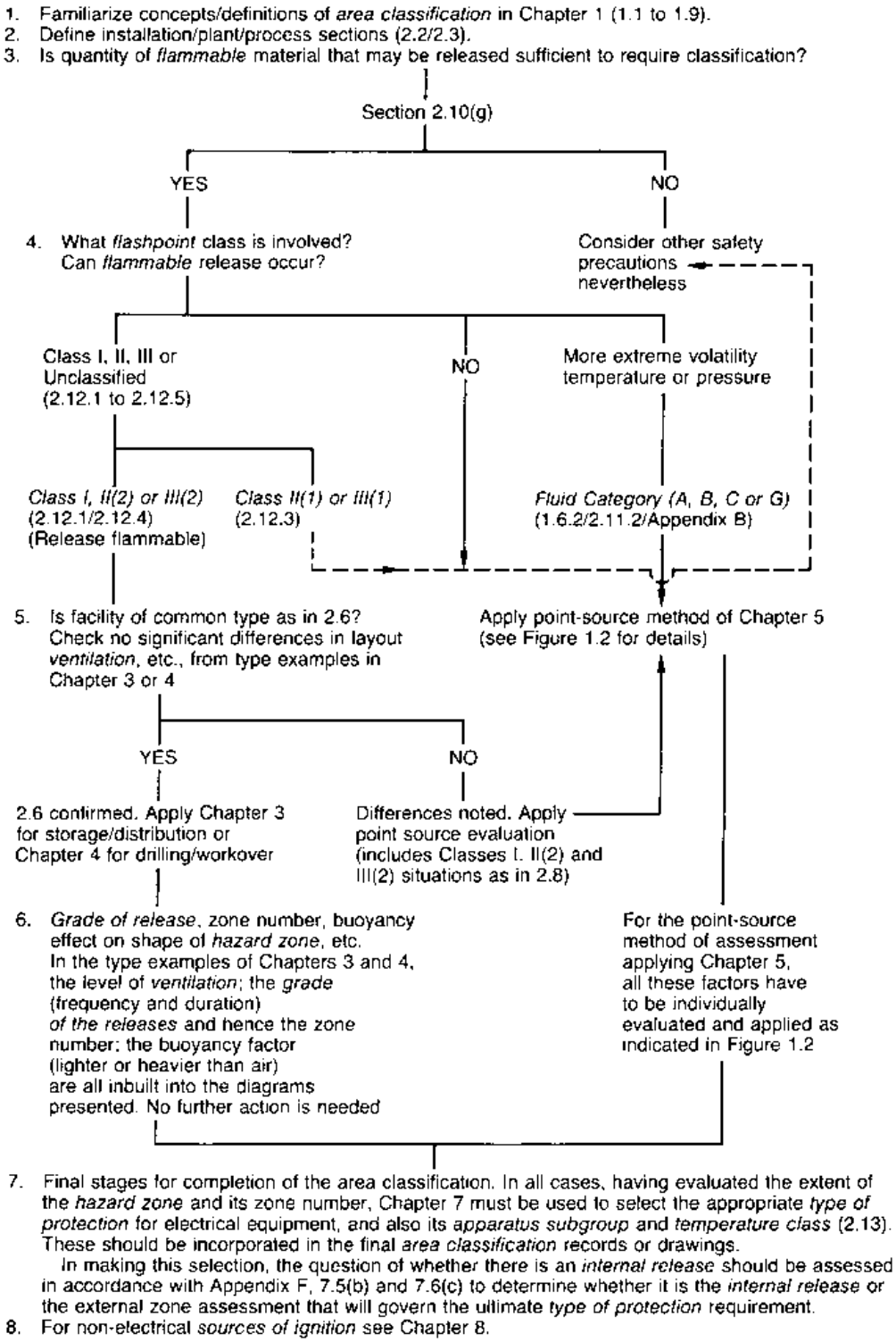


Figure 16.65 *Hazardous area classification – IP Area Classification Code (IP, 1990 MCSP Pt 15): decision tree for application of the code (Courtesy of the Institute of Petroleum; reproduced with permission)*

a blanket Zone 2 and the secondary grade sources, or groups of sources, must then be addressed individually. A Zone 1 area will often be surrounded in practice by a Zone 2 area, but there is no general requirement for this. Within a hazardous area, the designation of small areas as non-hazardous should be avoided. Hazardous area classification is not sufficiently precise to warrant this.

Classification by method of direct example

The basic method of classification, the method of direct example, is described in Chapter 3 of the IP *Code*.

There are on petroleum installations some arrangements of equipment which are so common that it is possible to give exemplars of the zonings to be used. The zoning of the relevant exemplar is applicable to an installation which does not differ significantly from it. Differences which may be significant may be associated with the fluid, the type of equipment, the operating conditions, the plant layout and/or the ventilation. If a significant difference exists, use should be made of the point source method.

For this method examples are given for Classes I, II(2) and III(2) for: (1) storage tanks, both fixed and floating roof, in the open, (2) road tanker loading, (3) road tanker discharge, (4) rail car loading, (5) marine facilities and jetties, (6) drum filling in the open, (7) filling and service stations and (8) certain bulk pressurized liquefied petroleum gas (LPG) installations.

Figure 16.66 shows the zoning recommended in the code for four storage tank configurations. Figure 16.66(a) is a cone or dome roof tank; Figure 16.66(b) a floating roof tank; Figure 16.66(c) a cone roof tank with an outer protective wall; and Figure 16.66(d) a floating roof tank with an outer protective wall.

Chapter 4 of the code extends the method of direct example by giving exemplars for drilling rigs and other petroleum production systems.

Classification by point source method

The alternative method of classification, the point source method, is described in Chapter 5 of the IP *Code*.

The process plant will generally consist of a Zone 2 area with Zone 1, and occasionally Zone 0, areas within this. The point source method is applied to potential sources of release to determine for each whether it should be assigned a Zone 1 or Zone 0 envelope and whether it affects the boundary of the Zone 2 area.

The method involves identifying for each point source (1) the grade of release and (2) the extent of the hazard zone, or hazard radius.

The grade of release determines the zone to be assigned: Zone 0 for continuous grade, Zone 1 for primary and Zone 0 for secondary for open air conditions, with adjustment of the severity of the zone for poor or very good ventilation.

The extent of the hazard zone is determined by the mass released and the fraction forming a gas or vapour cloud and by the conditions which affect the dispersal of the cloud, that is its buoyancy and the ventilation at that location. The hazard zone is characterized in terms of the hazard radius. The hazard radius of a source is defined as 'the largest horizontal extent of the hazardous area which is generated by the source when situated in an open area'. The *Code* gives guidance in Appendix C on the assessment of buoyancy and in Appendix D on the derivation of the hazard radius.

The *Code* treats a number of common types of point source, including the following: (1) pumps, (2) compressors, (3) piping systems, (4) drains and liquid sample points, (5) process and instrument vents, (6) liquid pools due to spillage, (7) sumps, interceptors and separators, (8) pig receivers and launchers and (9) surface water drainage systems.

The general approach taken is illustrated by the following examples. For pumps, for the case where the pump can be treated as a single point source, the hazard radius (m) is given as:

Fluid category	*Standard pump*	*High integrity pump*
A	30	7.5
B	15	3
C	7.5[a]	3

[a] For clean fluids, e.g. finished products which are pumped from atmospheric storage at rates not exceeding 100 m^3/h, the hazard radius may be reduced to 3 m.

For drains and liquid sample points the hazard radius (m) is:

Fluid category	*Diameter*[a] (mm)			
	3	*6*	*12*	*25*
A	7.5	15	30	–[b]
B	3	7.5	15	30
C	0.3	1.5	1.5	3

[a] Diameter of smallest item on drain or sample line, i.e. line, valve or restrictor.
[b] The size of release is greater than is normally considered in hazardous area classification, the hazard radius being greater than 30 m.

Elimination or modification of sources

As far as practical, features which pose problems in hazardous area classification should be eliminated or mitigated by changes in plant layout. In particular, (1) continuous or primary grades releases in less ventilated conditions should be avoided and (2) the creation of sheltered areas by obstructions should be minimized.

Ventilation

As the foregoing treatment indicates, ventilation affects the extent of the hazard zone. For artificial ventilation it may also affect the severity of the zone.

The IP *Code* takes as it starting point the types of ventilation given in IEC 79–10, which are (1) natural ventilation, (2) general artificial ventilation and (3) local artificial ventilation. IEC 79–10 recognizes two situations in which natural ventilation occurs. These are (1) open locations typical of process plant located outside and (2) open buildings in which the size and positioning of the openings is such as to give an equivalent degree of ventilation.

The IP *Code* treats ventilation in terms of the following situations: (1) 'open areas', (2) less ventilated conditions, which include (2a) sheltered areas and (2b) enclosed areas.

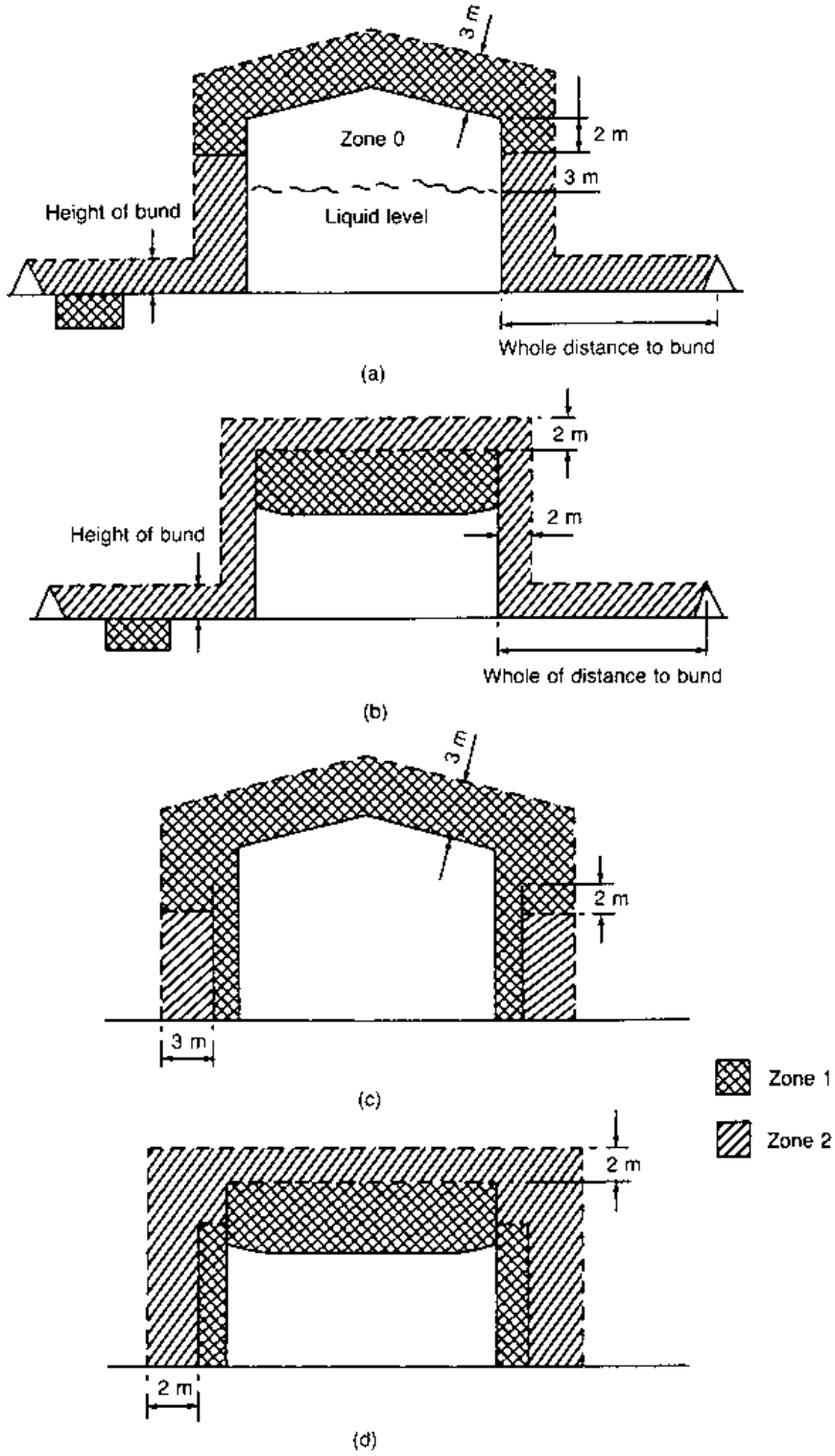


Figure 16.66 *Hazardous area classification – IP Area Classification Code (IP, 1990 MCSP Pt 15): zoning for storage tanks for Class I, II(2) and III(2) flammable liquids. (a) Cone or dome roof tank; (b) floating roof tank; (c) cone roof tank with outer protective wall; and (d) floating roof tank with outer protective wall. See Code for notes and qualifications (Courtesy of the Institute of Petroleum; reproduced with permission)*

The *Code* gives detailed guidance on what can be considered an open area. Essentially this is an open situation, which for land-based locations means that the wind velocity is rarely less than 0.5 m/s and is frequently greater than 2 m/s.

With regard to less ventilated conditions, it distinguishes between locations where the sheltered or enclosed area itself contains a source of release and those where it merely abuts an area containing, or lies within the hazard zone of, such a source. In both cases the severity of the zoning depends on the degree of ventilation. For less ventilated conditions, the *Code* utilizes the concept of 'adequate ventilation', defined as: 'the achievement of a uniform ventilation rate of at least twelve air changes an hour with no stagnant areas'.

If a less ventilated location has adequate ventilation through natural ventilation, it may be treated as a sheltered area. Otherwise, it must be treated as an enclosed area. Guidance on the classification of sheltered areas, with natural ventilation, is given in the *Code* which also describes a number of examples.

An enclosed area is one which in the absence of artificial ventilation has inadequate ventilation. The *Code* gives guidance on the classification of enclosed areas, utilizing the distinction between those with and those without an internal source of release.

An enclosed area requires artificial ventilation, which the *Code* treats in terms of the following three categories: (1) 'adequate' ventilation, (2) dilution ventilation and (3) overpressure ventilation.

The *Code* distinguishes between adequate ventilation and dilution ventilation. As already stated, adequate ventilation exists if there is an assurance of at least 12 air changes per hour. It is not related to the size of any potential release which may occur. If there is a release, adequate ventilation may not be sufficient to prevent the build-up of a flammable atmosphere, but on termination of the release it will be sufficient to prevent the persistence of such an atmosphere.

Dilution ventilation, by contrast, is intended to prevent a release giving rise to a flammable atmosphere and is therefore a function of the size of the potential release. It should be such that even immediately after a release the area can be considered as non-hazardous. The design criterion is that the flammable concentration should not rise above 20% of the lower flammability limit.

In some cases, particularly where there is a source of release in a large area, local artificial ventilation, typically utilizing a hood, may be used either to obtain local dilution ventilation or to restrict the extent of a Zone 1 area.

Another form of ventilation is pressurization, or overpressure ventilation. In this method an overpressure is maintained in the space so that flammable gas is excluded. The *Code* recommends an overpressure of at least 5 mm WG (50 Pa). This form of ventilation is not used where there is a source of release inside the enclosed area.

Figure 16.67 shows the decision tree given in the *Code* for the determination of ventilation.

Where artificial ventilation is provided for an enclosed area, consideration should be given to possible stagnant areas. Where these exist, possible countermeasures may include additional ventilation and gas detectors. It is necessary to consider what precautions should be taken to deal with the possibility of loss of artificial ventilation. The appropriate measures will depend on the particular situation. They may be aimed at reducing the frequency of failure, such as the installation of stand-by fans with separate power supplies and/or mitigating its consequences, such as the provision of gas detectors.

Selection and location of electrical equipment

The IP *Code* deals in Chapter 7 with the selection and location of electrical equipment, covering much the same ground as Section 16.8. The table showing the types of protection available has already been given in the previous section as Table 16.43.

The *Code* makes a distinction between electrical apparatus without and that with potential for internal release of flammable material. Certain types of instrument come into the latter category. Guidance on such apparatus is given in Appendix F of the *Code*.

Control of non-electrical ignition sources

Chapter 8 of the IP *Code* deals with the control and location of ignition sources other than electrical equipment. A hazardous area should preferably contain no fixed sources of ignition and close control should be exercised over any mobile ignition sources. In respect of mobile ignition sources, the *Code* deals mainly with permit-to-work systems and with the use of gas detectors.

Specific ignition sources the control of which is considered in the code include (1) hot surfaces, (2) furnaces and fired heaters, (3) combustion engines, (4) turbines, (5) road and rail traffic and (6) flares. Consideration is also given to pyrophoric and electrostatic hazards and air intakes.

16.9.4 API RP 500

The approach described in API RP 500: 1991 is broadly similar to the method of direct example just described. The code utilizes the NFPA classification of fluids given in Chapter 10 and the NFPA classification of hazardous locations and grouping of atmospheric mixtures given in Section 16.8. It distinguishes between outdoor and enclosed locations.

The *Code* gives exemplars of zoning in Section A for petroleum refineries; in Section B for production facilities, on land and offshore; and in Appendix C for petroleum pipelines.

The criterion given in the *Code* for 'adequate ventilation' is 6 air changes per hour. Appendices A-C of the *Code* deal with ventilation. They treat, respectively, (1) ventilation of an enclosed area by natural means, (2) ventilation for fugitive emissions and (3) development of ventilation criteria.

16.9.5 Quantification in hazardous area classification

The methods used in the codes just described are based essentially on industry experience supplemented by estimates of the frequency and range of releases. An indication that traditional approaches have tended to yield disparate results is given in Figure 16.68 (A.W. Cox, Lees and Ang, 1990). The figure shows the zoning recommendations of selected codes for certain common items.

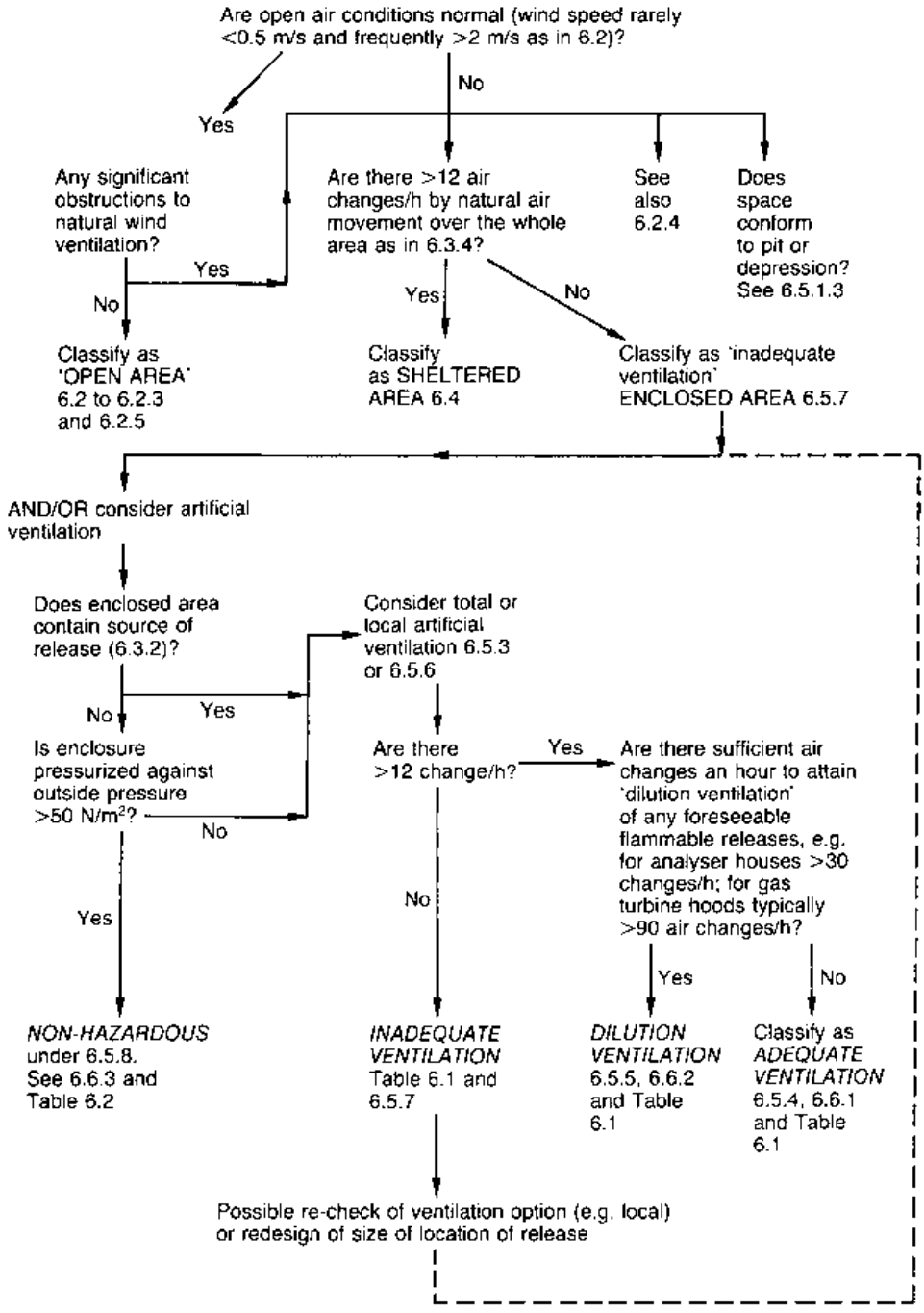


Figure 16.67 *Hazardous area classification – IP Area Classification Code (IP, 1990 MCSP Pt 15): decision tree for ventilation. This figure applies to facilities not covered in Chapters 3 and 4 of the code (Courtesy of the Institute of Petroleum; reproduced with permission)*

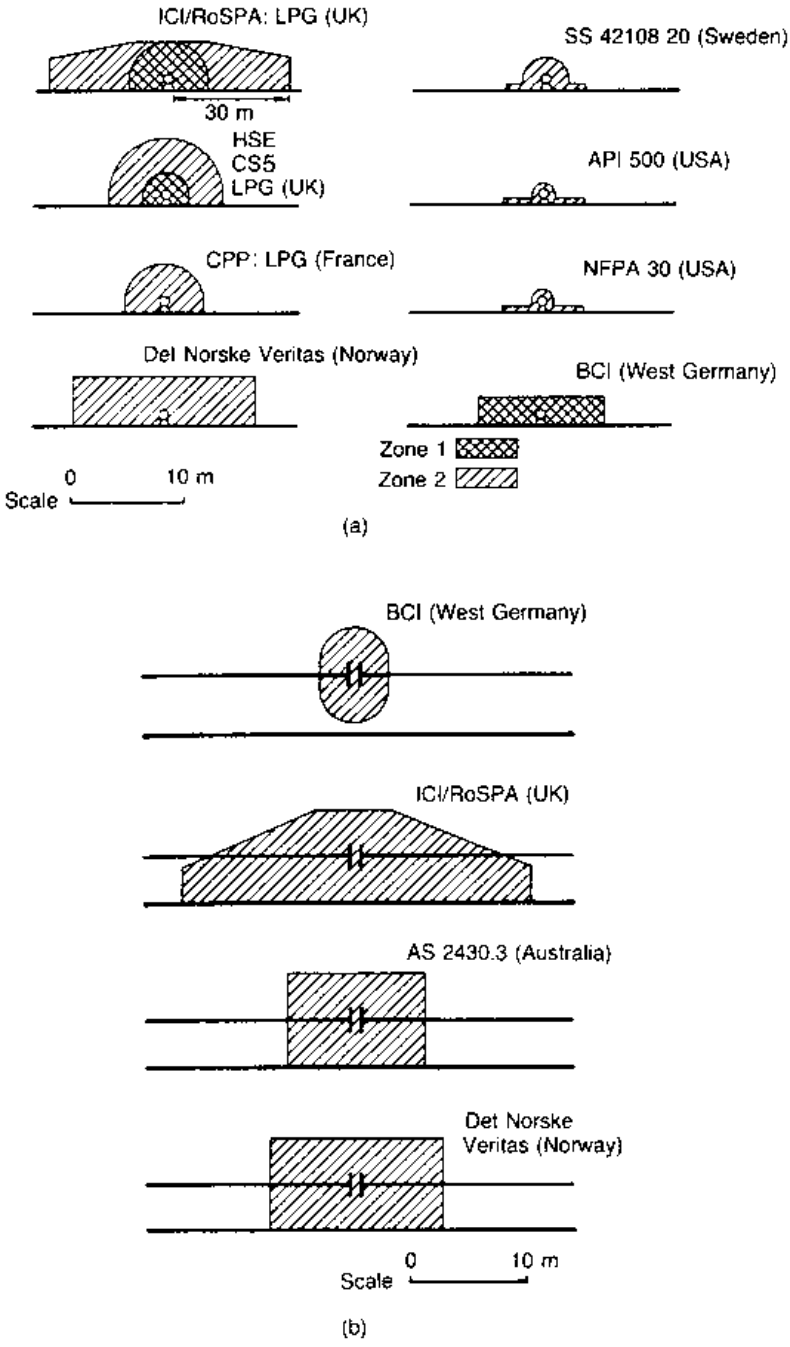


Figure 16.68 *Hazardous area classification: zone distances given by selected codes (A.W. Cox, Lees and Ang, 1990): (a) zone distances for pumps for LPG; (b) zone distances for flanges of pipework handling LPG; and (c) zone distances for storage tanks (Courtesy of the Institution of Chemical Engineers)*

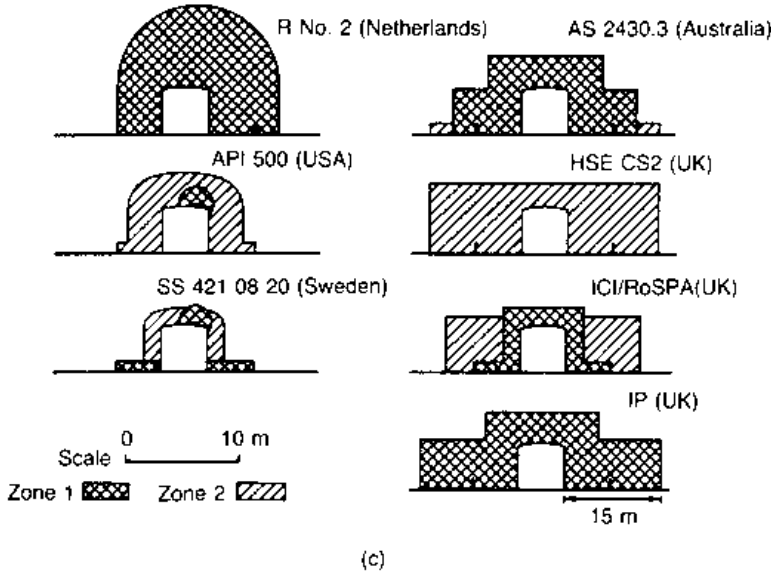


Figure 16.68 *continued*

One approach to hazardous area classification is: to identify particular types of source of release; to assign to each source a typical release rate, or set of rates; to assign to each release rate a frequency; to estimate the range of the release; and to use this release range to determine, for purposes of zoning, a hazard range. The estimation of the release range may be based on the modelling of flow, vaporization and dispersion. The estimation of frequency and the determination of the hazard range may be a matter of judgement.

This basic approach may be applied in one of two ways. One is to perform the whole exercise afresh for each source of release on each occasion that such a source is encountered in the design. The other, and more practical, way is to do the assessment once and for all and then to produce guidelines.

Approaches on these lines evidently inform some of the methods used in the codes just described, such as the source of hazard method of the ICI *Electrical Installations Code* and the point source method of the IP *Area Classification Code*.

A method based on the examination of individual leak sources has the advantage that it forces the engineer to identify these sources and to examine them more closely. It takes full account of the properties of the fluids and the operating conditions. It allows for engineering features designed to reduce the risk. It should give greater reassurance that the zone distances are right. On the other hand, there is a view that this approach can lead to much effort for little return, the end result often being little different from that obtained using a more general approach.

Hazardous area classification has not to date been based on any formal quantitative risk assessment. There have been different views on whether or not this is necessary. In any event, in this particular field quantification has proved difficult. Foremost among the problems is the lack of data on the basic frequency and size distribution of leaks for different potential sources. Uncertainties in modelling have been another significant factor.

Several parties have addressed the modelling aspect. In the mid-1980s a draft appendix to BS 5345 was produced which contained a collection of models for use in hazardous area classification, but this did not see the light of day. A discussion of such models has been given by O'Shea (1982). Another set of models are those given for plant layout by Mecklenburgh (1985), as described in Chapter 10. A set of models for natural gas is given in the British Gas in-house code BGC/PS/SHA1.

Research in support of a more quantitative approach has been described in *Classification of Hazardous Areas* by A.W. Cox, Lees and Ang (1990). This work involved the development and refinement of estimates of (1) the frequency and size distribution of leaks from typical leak sources, (2) the probability of ignition of the release and (3) the probability of explosion given ignition. An account of this ignition model is given in the next section. The authors state that the provision of these data provides the basis for the development of guidance based on quantitative risk assessment. They suggest that quantitative guidance might be formulated by exploring representative scenarios of release on plant layouts incorporating typical equipment, and sources of release, using a three-dimensional computer-aided design (CAD) plant layout code, utilizing the data on release frequency and size and ignition on which the ignition model is based, together with other data such as the probability of exposure of personnel.

16.10 Ignition Models

It is frequently necessary in hazard assessment to estimate the probability of ignition and of explosion if a leak occurs. There is therefore a requirement both for ignition models and for data from which to determine the parameters in such models. This is, however, an area where there is relatively little guidance available.

Information relevant to the modelling of ignition sources has been given in *Classification of Hazardous Areas*, the study by A.W. Cox, Lees and Ang (1990) already mentioned. This work includes a model for leaks of flammable fluids and for their ignition and explosion.

16.10.1 Modes of ignition

Ignition of a leak may occur either at the point of leak or at some distance from it. The cause of ignition may be the leak event itself or an ignition source. These distinctions may be illustrated by the following examples. A leak may occur at a pump seal which has failed due to a bearing failure and the hot bearing may ignite the leak. A leak may occur due to equipment rupture and the rupture may give a spark which ignites the leak. A leak may generate static electricity which then gives an incendive spark and ignites the leak. All these cases are treated here as ignitions by the leak event itself, regardless of how close to the point of leak ignition occurs.

It is usually convenient to consider a limited number of specific ignition sources and to treat the large number of other potential ignition sources as background sources. A specific ignition source may be present continuously or only intermittently.

From the foregoing, the modes of ignition may be classified as follows:

(1) event ignition;
(2) specific ignition source –
  (a) continuous,
  (b) intermittent;
(3) background ignition.

It may also be helpful to distinguish between those ignition sources on which action is practical when a gas alarm occurs and those for which it is not.

16.10.2 Distribution of ignition sources

Some data on the distribution of ignition sources onshore are given in Table 16.46. These data are from a survey by Cox, Lees and Ang of incidents reported to the Health and Safety Executive (HSE).

Information on ignition sources offshore has been given by Sofyanos (1981) and by Forsth (1981a,b, 1983). Table 16.47 shows data given by Forsth (1983) for the Gulf of Mexico (GoM) and for the Norwegian North Sea (NNS). The number of accidents considered was 326 in the GoM over the period 1956–82 and 133 in the NNS over an unspecified period.

16.10.3 Probability of ignition

The information available on the probability of ignition is mostly in the form of expert estimates. In the context of vapour cloud explosions, Kletz (1977j) states that on polyethylene plants the leaks are mostly very small and that about one leak in 10 000 ignites, due probably to good jet mixing with air. He also states that on a series of plants handling a hot mixture of hydrogen and hydrocarbons about one leak in 30 ignites. He argues that the probability of ignition increases with the size of leak and suggests that for large leaks (>10 ton) the probability of ignition is greater than 1 in 10 and perhaps as high as 1 in 2.

R.L. Browning (1969c) has given a set of estimates of the relative probabilities of ignition. For ignition under conditions of no obvious source of ignition and with explosion-proof electrical equipment he gives the following probabilities of ignition:

	Relative probability of ignition
Massive LPG release	10^{-1}
Flammable liquid with flashpoint below 110°F or with temperature above flashpoint	10^{-2}
Flammable liquid with flashpoint 110–200°F	10^{-3}

Elsewhere R.L. Browning (1980) gives a table of probabilities which are evidently absolute probabilities. The table includes an estimate of the probability of ignition of flammable gas–liquid spills of 10^{-2}–10^{-1}.

The First *Canvey Report* (HSE, 1978b) gives for LNG vapour clouds:

	Probability of ignition
Limited releases	10^{-1}
Large releases	1

Table 16.46 *Ignition sources in fire and explosion survey of national case histories (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

	No. of incidents	*Proportion of incidents* (%)	
		Unadjusted	*Adjusted*[a]
Flame:			
general	8	9.3	16.7
LPG fired equipment	2	2.3	4.1
Hot surfaces	10	11.6	20.8
Friction	4	4.7	8.4
Electrical	8	9.3	16.7
Hot particles	3	3.5	6.3
Static electricity	6	7.0	12.5
Smoking	–	–	–
Auto-ignition	7	8.1	14.5
Unknown	38	44.2	–
Total	86	100.0	100.0

[a] Adjusted figures are based on eliminating the unknown category and redistributing the known ignition sources in their original relative proportions.

Table 16.47 *Ignition sources for fires and explosions on offshore platforms in the Gulf of Mexico 1956–81 and the Norwegian North Sea (A.W. Cox, Lees and Ang, 1990; after Forsth, 1983) (Courtesy of the Institution of Chemical Engineers)*

	Proportion of incidents[a] (%)			
	NNS		*GoM*	
	Unadjusted	*Adjusted*	*Unadjusted*	*Adjusted*
Welding/cutting/grinding	18	–	59	–
Engines and exhausts	34	50.7	4	14.3
Sparks	4	6.0	1	3.6
Electrical	16	23.9	9	32.0
Hot surfaces[b]	0	0	6	21.4
Self-ignition	1	1.5	1.5	5.4
Cigarette, lighter, match	1	1.5	1.5	5.5
Other	11	16.4	5	17.9
Unknown, not reported	17	–	12	–
Total		100		100

GoM, Gulf of Mexico; NNS, Norwegian North Sea.
[a] Adjusted figures are based on eliminating the hot work and unknown categories and redistributing the known ignition sources in their original relative proportions.
[b] Other than engines and exhausts.

Table 16.48 *Probability of ignition and of explosion for offshore blowouts (A.W. Cox, Lees and Ang, 1990; after Dahl et al., 1983) (Courtesy of the Institution of Chemical Engineers)*

A Probability of ignition

Blowout fluid	No. of blowouts	No. of ignitions	Probability of ignition
Gas	123	35	0.3
Oil	12	1	0.08

B Probability of explosion, given ignition

Blowout fluid	No. of blowouts	No. of ignitions	No. of explosions	Probability of explosion given ignition
Gas	123	35	12	0.34
Oil	12	1	0	0

The Second *Canvey Report* (HSE, 1981a) gives the following 'judgment' values for ignition on site:

Ignition sources	*Probability of ignition*
'None'	0.1
Very few	0.2
Few	0.5
Many	0.9

For offshore locations, Dahl *et al.* (1983) have analysed ignition data for gas and oil blowouts, which may be regarded as massive releases. The data are shown in Table 16.48, Section A. They cover both drilling rigs and production platforms. The overall probability of ignition of blowouts is similar for the two cases.

Table 16.49 *Estimates of probability of ignition for leaks of flammable fluids (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

Leak	*Probability of ignition*	
	Gas	*Liquid*
Minor (< 1 kg/s)	0.01	0.01
Major (1–50 kg/s)	0.07	0.03
Massive (> 50 kg/s)	0.3	0.08

Cox, Lees and Ang draw on the foregoing to make estimates of the probability of ignition. They define a minor leak as one <1 kg/s and take for this an average leak flow of 0.5 kg/s. They define a massive leak as one >50 kg/s and take for this an average leak flow of 100 kg/s. They estimate the probability of ignition of a minor leak of either gas or liquid as 0.01, that of a massive leak of gas as 0.03 and that of a massive leak of liquid as 0.08. From these estimates they derive those given in Table 16.49 and Figure 16.69.

16.10.4 Probability of explosion

The information available on the probability of explosion is also mostly in the form of expert estimates. In his account of vapour cloud explosions, Kletz (1977j) has also given estimates of the probability of explosion. He quotes the following figures:

Frequency of serious vapour cloud fires = 5/year
Frequency of serious vapour cloud explosions = 0.5/year

and derives from these for a large vapour cloud

Probability of explosion given ignition = 0.1

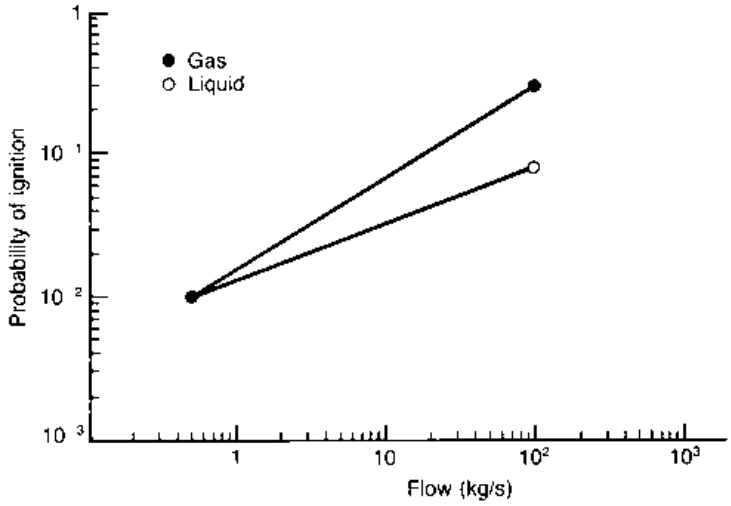


Figure 16.69 *Estimated probability of ignition for leaks of gas or liquid (A.W. Cox, Lees and Ang, 1990). (—) Initial estimates, which were used unaltered in the ignition model – see text (Courtesy of the Institution of Chemical Engineers)*

Table 16.50 *Probability of explosion given ignition for blowouts in the Gulf of Mexico (A.W. Cox, Lees and Ang, 1990; after Sofyanis, 1981) (Reproduced by permission of the Institution of Chemical Engineers)*

Damage category[a]	*No. of incidents with fire and explosion*	*No. of incidents with explosion only*	*Probability of explosion given ignition*
I	9	5	0.55
II	13	3	0.23
III	33	6	0.18
IV	128	22	0.18
V	143	6	0.042
Total	326	42	0.13[b]

[a] The damage categories are in decreasing order of severity, Category I being loss of platform and Category V being an incident of no consequence.
[b] Weighted average.

He also gives estimates which are evidently for the probability of explosion given leak. These are a probability >0.1 for a large vapour cloud (>10 ton) and 0.001–0.01 for a medium vapour cloud (1 ton or less).

The First *Canvey Report* gives for a refinery

Probability of explosion, given major fire = 0.5

and for large LNG vapour clouds

	Probability of explosion given ignition
Large vapour clouds	1
Smaller clouds of gases other than methane	0.1
Smaller clouds of methane	0.01

For offshore locations, Dahl *et al.* (1983) have analysed blowouts as shown in Table 16.48, Section B.

Sofyanos (1981) has given for fires and explosions in the Gulf of Mexico the data shown in Table 16.50.

For the estimation of the probability of explosion, Cox, Lees and Ang used for massive leaks the value of 0.3 given by Dahl *et al.* for blowouts and for minor leaks the value of 0.04 given by Sofyanos for Category V leaks. From these estimates they derive those given in Table 16.51 and Figure 16.70.

16.10.5 Distribution of leaks

In order to model the occurrence of fire and explosion on a plant it is also necessary to have information on the frequency of leaks. Table 16.52 gives the estimates of leak frequency used by Cox, Lees and Ang.

16.10.6 Cox, Lees and Ang model

The approach taken by Cox, Lees and Ang is to define an equivalent standard plant and to make for this plant estimates of the frequency of leaks of flammable gas and liquid and of ignitions and explosions. The inventory of

Table 16.51 *Estimates of probability of explosion given ignition for leaks of flammable gas (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

Leak	*Probability of explosion given ignition*
Minor (< 1 kg/s)	0.04
Major (1–50 kg/s)	0.12
Massive (> 50 kg/s)	0.3

equipment in the equivalent standard plant (ESP) is listed in Table 16.53.

These various data sets are then combined to give a model, described by the authors as a fire and explosion model, but referred to here as an ignition model. From the inventory of equipment on the ESP and the generic estimates of leak frequency the frequency of leaks on the plant is obtained. The frequency of fire and explosions is then obtained from the ignition and explosion probabilities shown in Figures 16.69 and 16.70.

The data in Tables 16.52 and 16.53 and Figures 16.69 and 16.70 used in the model were initially obtained as independent estimates, but were then adjusted to give a better fit to the historical data such as the frequency of plant fires and vapour cloud explosions. For the leak frequency the original estimates are shown in Table 16.52 in brackets. No adjustment was made to the ignition probabilities given in Table 16.49 and Figure 16.69, but the explosion probabilities given in Table 16.51 and Figure 16.70 were adjusted to:

Leak	*Probability of explosion given ignition*
Minor (<1 kg/s)	0.025
Massive (>50 kg/s)	0.25

If, therefore, the estimate of the probability of explosion is based on the outcome from the model rather than on those derived in Section 16.10.4, the values given by the dotted line in Figure 16.70 apply.

Some results obtained by running the model for the equivalent standard plant are given Table 16.54. Leak, fire and explosion frequencies are given in Section A of the table by leak source and in Section B by fluid phase. The authors give comparisons of these results with historical data on fires and vapour cloud explosions, both overall and by leak source and fluid phase.

The purpose of the model as developed by the authors is to provide a check on the estimates of leak frequency. The conventional approach in hazard assessment is to make estimates of frequency and to derive confidence limits on these estimates. For leaks, however, the data appeared to be too sparse to permit this approach. The problem was therefore tackled in a different way. The estimates of leak size distribution and frequency were used to make, for a typical plant, estimates not only of the overall frequency of fire and explosion but also of leaks by leak size, by fluid phase and by leak source, and hence of the distribution of leaks by size, fluid phase and leak source. Thus the model may be tested in terms not only of the final results but also of a number of intermediate results. For example, not only should the overall frequency of explosions accord with historical values, but so should the distribution of explosions by leak source. The totality of such comparisons constitutes a relatively robust cross-check. It is this conceptual approach which is the main value of the model.

16.10.7 Models utilizing dispersion relations

The model just described utilizes the overall probability of ignition expressed as a function of the leak flow. The characterization of ignition probability may be extended by modelling the physical basis for the relation between it and the leak flow.

Some features which such a model should possess are given by Cox, Lees and Ang as follows:

(1) the effect of the fluid phase, gas or liquid, should be taken into account;
(2) the probability of ignition for an unprotected location should increase as the leak flow increases;

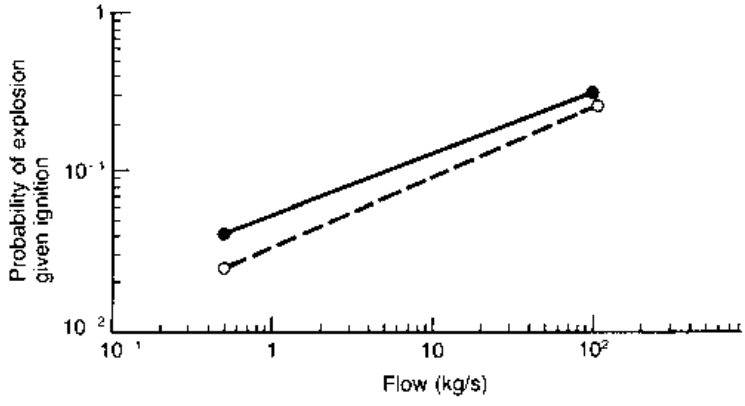


Figure 16.70 *Estimated probability of explosion given ignition for leaks of gas (A.W. Cox, Lees and Ang, 1990): (—) Initial estimate; and (– – –) estimate used in the ignition model – see text (Courtesy of the Institution of Chemical Engineers)*

(3) there should be a finite probability of ignition which allows for the failure to achieve perfect protection even within the designated zones, and this probability also should increase as the leak flow increases;
(4) there should be a finite probability of event ignition;
(5) the estimated probability of ignition should be the sum of (3) and (4) over the range covered by zoning and of (2) and (4) over the range not so covered.

The overall probability of ignition and the probability of event ignition estimated from the model should both be in broad agreement with that observed.

The leak flow determines the distance, and hence the area covered or volume encompassed by the leak. This area or volume may be obtained using suitable emission and dispersion relations. A model for the probability of ignition may then be constructed in which the probability is a function of the area or volume, depending on the situation considered.

One outcome of such an approach is the speculative model shown in Figure 16.71. Line A gives the estimated probability of ignition given a normal, partial degree of protection against ignition and corresponds to the line given in Figure 16.69. Lines B and C represent the component parts of line A, line C being the part due to event ignition and line B that due to ignition sources, both specific and background. Line D gives the estimated probability of ignition assuming no protection. Line E illustrates a possible actual curve for ignition probability.

Critical features of such a model are the probabilities of event ignition and the slope of the lines derived on the one hand from estimates of overall probability of ignition and on the other from the dispersion models.

16.10.8 Models with specific ignition sources

The matter can be taken further by expressing the overall probability of ignition as a function of the contributions of the various ignition sources. For this purpose it is convenient to utilize the classification given in Section 16.10.1 and to write the overall probability of ignition P as a function of the probability P_a of ignition by the event itself, or event ignition, of the probability P_b

Table 16.52 *Estimates[a] of leak frequency used in ignition model (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

A Pipework: leak frequency (leaks/m yr)

	Pipe diameter (m)			
	0.025	*0.050*	*0.100*	*0.300*
Rupture leak	0.005 (0.01)	0.005 (0.01)	0.0015 (0.003)	0.0005 (0.001)
Major leak	0.05 (0.1)	0.05 (0.1)	0.015 (0.06)	0.005 (0.03)
Minor leak	0.5 (1)	0.5 (1)	0.15 (0.3)	0.05 (0.1)

B Flanges (all pipe diameters): leak frequency (leaks/yr)

Major leak	0.3 (1)
Minor leak	3 (10)

C Valves: leak frequency (leaks/yr)

	Pipe diameter (m)			
	0.025	*0.050*	*0.100*	*0.300*
Rupture leak	0.01 (0.1)	0.01 (0.1)	0.01 (0.1)	0.005 (0.1)
Major leak	0.1 (1)	0.1 (1)	0.1 (1)	0.05 (1)
Minor leak	1 (10)	1 (10)	1 (10)	0.5 (10)

D Pumps (all pipe diameters): leak frequency (leaks/yr)

Rupture leak	0.3 (0.3)
Major leak	3 (3)
Minor leak	30 (30)

E Small bore connections: leak frequency (leaks/yr)

	Pipe diameter = *0.01* m
Rupture leak	1 (5)
Major leak	10 (50)

[a] All values to be multiplied by 10^{-4}.

Table 16.53 *Inventory of leak sources on equivalent standard plant used in ignition model (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

A Pipework, flanged joints, valves

Pipe diameter (mm)	*Pipe length*		*Flanged joints*	*Valves*	*Proportion on gas (%)*
	(m)	*(%)*			
15	525	3.5	100	120	0
20	90	0.6	200	100	0
25	3000	20.0	600	500	0
40	2100	14.0	420	200	5
50	2100	14.0	650	300	8
80	3300	22.0	530	140	8
100	1050	7.0	160	60	8
150	1050	7.0	120	40	8
200	600	4.0	100	18	10
250	300	2.0	55	10	20
300	150	1.0	30	5	20
350	45	0.3	5	2	20
400	525	3.5	20	3	20
450	45	0.3	5	–	20
500	120	0.8	5	2	20
Total	15 000		3000	1500	

B Pumps

No. of pumps = 25

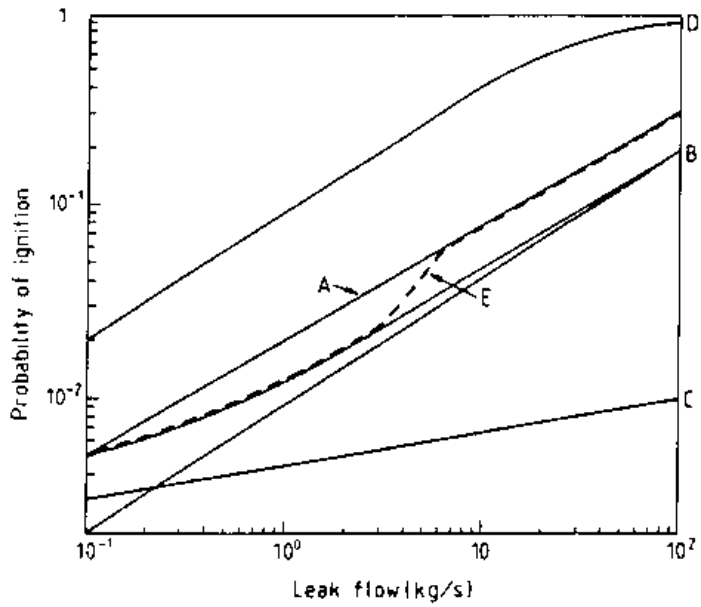


Figure 16.71 *Speculative model for the probability of ignition of leaks of flammable gas (after A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

Table 16.54 *Leak, fire and explosion frequencies obtained using the ignition model (A.W. Cox, Lees and Ang, 1990) (Courtesy of the Institution of Chemical Engineers)*

A By leak source

Flow (kg/s)	*<1*	*1–50*	*>50*	*Total*	*Proportion* (%)
Leak frequency (leaks/plant year)					
Pipework	0.422	0.115	0.00318	0.540	21.2
Flanges	0.910	0.080	0	0.990	38.9
Valves	0.130	0.340	0.00037	0.164	6.4
Pumps	0.045	0.038	0.00030	0.083	3.3
Small bore connections	0.711	0.060	0	0.770	30.2
Total	2.22	0.33	0.0038	2.55	
Proportion (%)	87.0	12.8	0.15		
Fire frequency[a] *(fires/plant year)*					
Pipework	42.7	31.3	5.82	80.0	25.9
Flanges	91.0	16.3	0	107	34.8
Valves	13.2	9.21	0.741	23.1	7.5
Pumps	4.50	9.02	0.504	14.0	4.5
Small bore connections	71.1	13.1	0	84.2	27.3
Total	222	79	7	308	
Proportion (%)	72.1	25.6	2.3		
Explosion frequency[a] *(explosions/plant year)*					
Pipework	0.431	1.42	1.10	2.95	48.0
Flanges	0.753	0.418	0	1.17	19.1
Valves	0.128	0.427	0.151	0.705	11.5
Pumps	0.027	0.281	0.090	0.398	6.5
Small bore connections	0.630	0.362	0	0.991	15.0
Total	1.90	2.90	1.34	6.14	
Proportion (%)	30.9	47.3	21.8		

[a] All values to be multiplied by 10^{-4}.

B By fluid phase

Flow (kg/s)	*<1*	*1–50*	*>50*	*Total*	*Proportion* (%)
Leak frequency (leaks/plant-year)					
Liquid	0.930	0.164	0.00184	1.10	43.0
Gas	0.285	0.00494	0.000026	0.29	11.4
Two-phase	1.00	0.157	0.00200	1.16	45.6
Total	2.22	0.326	0.0039	2.55	
Proportion (%)	87.0	12.8	0.15		
Fire frequency[a] *(fires/plant-year)*					
Liquid	93.0	32.4	1.46	127	41.1
Gas	28.6	1.7	0.077	30	9.8
Two-phase	101	44.9	5.53	151	49.1
Total	222	79	7.1	309	
Proportion (%)	72.0	25.6	2.3		
Explosion frequency[a] *(explosions/plant-year)*					
Gas	0.248	0.137	0.019	0.404	6.6
Two-phase	1.65	2.77	1.32	5.74	93.4
Total	1.90	2.90	1.34	6.14	
Proportion (%)	30.9	47.3	21.8		

[a] All values to be multiplied by 10^{-4}.

of ignition by a specific ignition source, and of the probability P_c of ignition by one of the background ignition sources, or background ignition:

$$P = f(P_a, P_b, P_c) \quad [16.10.1]$$

The overall probability of ignition is then

$$P = P_a + P_b + P_c - P_aP_b - P_aP_c - P_bP_c + P_aP_bP_c \quad [16.10.2a]$$

$$= P_a + P_b + P_c \qquad P_a, P_b, P_c \ll 1 \quad [16.10.2b]$$

The probability P_b of ignition by specific ignition sources is

$$P_b = 1 - \prod_{i=1}^{n}(1 - P_{b;i}) \quad [16.10.3a]$$

$$P_b = \sum_{i=1}^{n} P_{b;i} \qquad P_{b;i} \ll 1 \quad [16.10.3b]$$

where $P_{b;i}$ is the probability of ignition by ignition source i.

For a specific ignition source the probability of ignition is

$$P_{b;i} = P_{b;i;1}P_{b;i;2}P_{b;i;3}P_{b;i;4} \quad [16.10.4]$$

where

$P_{b;i;1}$ is the probability that the source is present, $P_{b;i;2}$ is the probability that the flammable region of the gas cloud reaches the source, $P_{b;i;3}$ is the probability that the source, if active, is able to ignite the gas, and $P_{b;i;4}$ is the probability that the source is active.

The probability $P_{b;i;1}$ depends on the plant configuration and zoning practices under consideration. Probability $P_{b;i;2}$ may be estimated using dispersion relations. Probability $P_{b;i;3}$ allows for the strength of the ignition source in relation to the strength required to ignite the cloud. Probability $P_{b;i;4}$ allows for the fact that the ignition source may be intermittent. The last two depend on the type of ignition source.

The model can accommodate different sets of specific ignition sources. From Tables 16.46 and 16.47 and from general considerations a suitable set might be

(1) flames;
(2) hot work;
(3) hot surfaces;
(4) electrical;
(5) engines, motors;
(6) human activity.

In making this selection, allowance has been made for the possibility of action when a gas alarm occurs. An engine may be shut down, but a hot exhaust will remain hot for a period. Broadly speaking, the items in this set on which action may be taken are hot work, engines and motors and human activity.

For the probability P_a of event ignition the offshore data given in Table 16.47 suggest an overall value of about 1–5%, say 3%. It may be expected that this probability will be higher for a large leak than for a small one.

Insofar as a model of this kind gives more detailed information about the specific ignition sources and their characteristics, it provides a basis not only for hazard assessment but also for taking action to reduce the probability of ignition.

16.10.9 Models in hazard assessment systems

Hazard assessment systems often include an ignition model. Other ignition models have been given in specific hazard assessments. Most of these models relate to ignition sources which might ignite a vapour cloud drifting beyond the plant boundary.

In the vulnerability model described by Eisenberg, Lynch and Breeding (1975), the occurrence of ignition is determined as follows. It is assumed that an ignition source is located at the centre of each population cell and that ignition occurs if a flammable mixture reaches such an ignition source. The type of ignition source is specified for each cell by the user, the two types giving fire or explosion, respectively.

The handling of ignition sources in the SAFETI package has been described by Ale and Whitehouse (1986) and Pitblado and Nalpanis (1989). As for population, a 100 m × 100 m grid is used, and ignition sources are located inside each grid. Point, line or areas sources may be specified. Each source has two attributes: the probability that it is active and the probability that it is effective. Day and night are treated as separate cases.

A somewhat different approach is used in the short-cut classical method (SCM) described by R.A. Cox and Comer (1982). There the probability P of ignition is assigned specified values at regular intervals of distance dr and is thus specified as a function of the direction θ and the distance r (= idr)

$$P = f(\theta, r) \quad [16.10.5]$$

Another approach, described by English and Waite (1989), is to assume a constant density μ of ignition sources. The probability increment δP of ignition for a sector of semi-angle θ_s at distance r is then

$$\delta P = \mu r \tan \theta_s \, \mathrm{d}r \quad [16.10.6]$$

and the probability P of ignition by the time a distance r has been reached is

$$P = 1 - \exp(-\theta_s \mu r^2) \quad [16.10.7]$$

The treatment of ignition sources in the *Rijnmond Report* is described in Appendix 8.

16.11 Fire in Process Plant

Fires in process plant are a serious hazard to both life and property. It is essential, therefore, to understand the ways in which fire can occur and develop.

Normally, fire occurs as a result of a leakage or spillage of fluid from the plant. Larger leaks may occur due to the failure of a vessel, pipe or pump, and smaller ones from flanges, sample and drain points and other small bore connections.

Combustion of material which has leaked from a plant may take a number of forms. A leak of gas or liquid may be ignited at the point of issue so that it behaves like a flame on a burner. In some circumstances this flame may be directed like a blow torch at another part of the plant.

If the leak gives rise to a gas or vapour cloud which grows for a period before it is ignited, the resultant effect may be either a vapour cloud, a flash fire, or a vapour

cloud explosion. Vapour cloud explosions are considered in Chapter 17.

In a flash fire the gas cloud burns, but does not explode. A typical flash fire may cause quite extensive damage, particularly to vulnerable items such as electric cabling, but may leave the main plant equipment relatively unharmed. However, a flash fire does cause a sudden depletion of oxygen, and this effect can be lethal to personnel.

If the leak forms a liquid pool on the ground, this may ignite and burn. The flame may be substantial and may do damage by direct impingement or by radiation. If the release results from fire engulfment of a vessel, a fireball may be formed.

Prevention of fire in process plant is primarily a matter of preventing leaks and avoiding sources of ignition. In addition to fires arising from leakage in general, there are certain characteristic types of fire on process plant. These include (1) pump fires, (2) flange fires, (3) lagging fires, (4) duct fires, (5) cable tray fires, and (6) storage tank fires. These various types of fire are now discussed.

16.11.1 Pump fires

Pumps tend to leak at the gland or the seal and the leakage frequently ignites causing a fire. Pump fires have been discussed by Kletz (1975b), who describes a number of incidents involving leakage and/or fire from seals on cold duty pumps on olefin separation plants. He quotes three cases of leaks from cold ethylene pumps. In one there was a leakage over 20 minutes of some 3 ton of vapour which formed a cloud, but blew away without igniting. In the other two there was ignition at the pump. The cause of ignition may have been static electricity. In both instances there was a jet of vapour containing liquid droplets. With C3 and C4 hydrocarbons at moderate pressure and ambient temperature, however, there are far fewer pump seal leak fires.

Kletz (1971) has also provided estimates made by experts of the frequency of fires on pumps with different duties. These estimates are given in Table 16.55. These accounts of pump fires are given by Kletz in the context of the use of emergency isolation valves to prevent a serious leak at the pump. The provision of such isolation arrangements is one of the principal means of mitigating pump fires. An alternative approach is to improve the mechanical reliability of the pump. The use of double mechanical seals, for example, greatly reduces the frequency of seal failure.

Table 16.55 *Estimated frequency of pump fires (after Kletz, 1971) (Courtesy of the Institution of Chemical Engineers)*

Material in pump	*Estimated frequency of fires* (fires/pump-year)
LPG below ambient temperature	$> 10^{-3}$
Material above autoignition temperature	$> 10^{-3}$
Flammable material well above ambient temperature (e.g. petrol at 70°C, gas oil at 150°C)	$< 10^{-3}$ $> 10^{-4}$
LPG at ambient temperature	$< 0.33 \times 10^{-3}$ $> 0.33 \times 10^{-4}$
Petrol or similar materials at or near ambient temperature	$< 10^{-4}$ $> 10^{-5}$
Gas oil or similar materials below their flashpoints	$< 10^{-5}$

A fire at a pump can do considerable damage. It is important, therefore, to assess the effect of a fire on equipment above the pump. In some fires the damage has been much reduced by a concrete floor above the pump alley.

Electrical and instrument cabling is particularly liable to be damaged by a pump fire. If such cabling is put out of action, the plant may be down for a much longer period than is required to deal with the fire itself. Methods are available for giving such cabling a 15–minute protection against fire, but they involve additional expense.

The provision of protection against pump fires is a good illustration of the loss prevention approach. The need for measures such as improved pump reliability, an emergency isolation valve or protected cabling, should be assessed by considering for each case the frequency and consequences of a pump fire.

16.11.2 Flange fires

Pipe flanges tend to leak and sometimes the leakage is ignited so that there is a fire. An account of flange fires and their prevention has been given by McFarland (1969). Leakage at flanges is induced mainly be temperature transients which put elements of the flange assembly under stress and may cause them to yield.

Figure 16.72 shows this effect for a normal gasketed joint. The joint is shown in Figure 16.72(a) as new, in Figure 16.72(b) during the passage of hot fluid when the temperature of the inside of the pipe is hotter than that of the outside and causes differential expansion, and in Figure 16.72(c) after the transient has caused yielding of the flanges and/or bolts and compression in the gasket.

A lens ring joint of the type which is self-tightening under pressure is illustrated in Figure 16.73. Figure 16.73(a) shows the joint as new and Figure 16.73(b) shows it after a sudden reduction in temperature has caused the joint ring to suffer radial strain and leak. Figures 16.73(c) and 16.73(d) indicate two possible solutions, the use of an insulating pad between the joint ring and the pipe bore, and the provision of a more massive flange.

Figures 16.74(a) and 16.74(b) show two other methods of improving the leak-tightness of an existing flanged joint: using longer bolts with sleeves and with Belleville washers, respectively. In the latter case it is necessary to ensure that the washers cannot lose temper due to high temperatures.

The main alternative hypothesis advanced to explain the Flixborough disaster involved a flange fire. The elbow of an 8 in. line showed evidence of having been subjected to a directed flame. It was suggested that a gasket blew on a non-return valve inside a lagging box near to the elbow and gave rise to an annular leak and off-port flame directed at the elbow.

16.11.3 Lagging fires

Lagging on plant equipment frequently becomes impregnated with oils and other liquids. If the lagging is hot, self-heating and ignition may occur, leading to a lagging

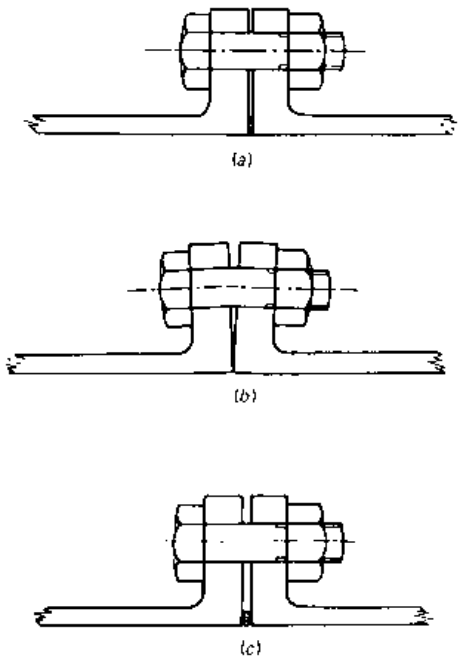


Figure 16.72 *A normal gasketed joint (after McFarland, 1969): (a) as new; (b) a hot fluid puts pipe under stress and causes bolts and flanges to yield; (c) when the fluid temperature falls, leakage can occur (Courtesy of the American Institute of Chemical Engineers)*

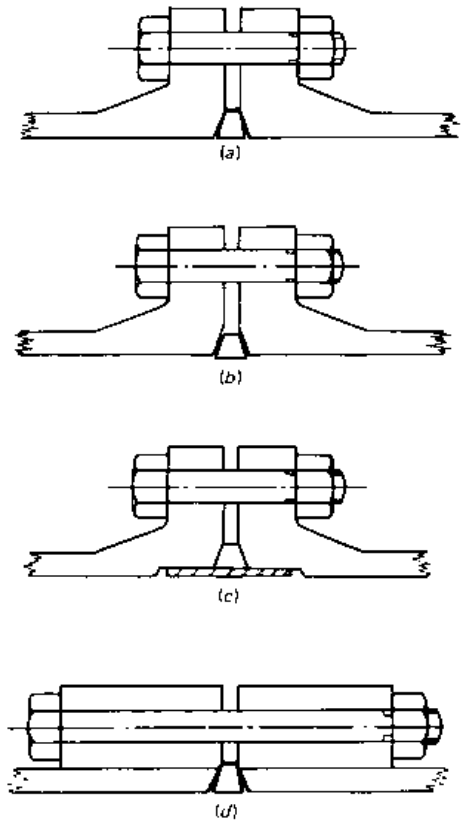


Figure 16.73 *A lens ring joint (after McFarland, 1969): (a) as new; (b) if there is a sudden temperature reduction the joint ring can suffer radial strain and leak; (c) addition of an insulating panel between the joint ring and the pipe bore reduces leakage; (d) use of more massive flanges gives better resistance to stress (Courtesy of the American Institute of Chemical Engineers)*

fire. In one small refinery the number of lagging fires in the period 1958–61 ranged from 14 to 21 per year (Petkus, 1964).

Lagging fires have been investigated by P.H. Thomas, Bowes and co-workers (e.g. P.H. Thomas, 1958; P.H. Thomas and Bowes, 1961a, 1967; Bowes and Langford, 1968; Bowes, 1974a, 1976) and by Gugan (1974a, 1976).

A lagging fire is essentially a self-heating phenomenon. Self-heating was discussed in Section 16.6. The design of insulation systems to minimize lagging fires has been considered in Chapter 12.

The conditions for a lagging fire to occur are that there should be sufficient fuel, oxygen and heat. Factors relevant to the occurrence of a fire are (1) oil, (2) leak, (3) insulation material, (4) insulation sealing, and (5) insulation geometry and temperature.

The most important factor in a lagging fire is the oil itself. For significant self-heating to occur the oil needs to be involatile (a volatile oil vaporizes too easily). An intrinsically reactive unsaturated oil is more prone to self-heating than is a saturated mineral oil, but any combustible involatile oil may self-heat.

Some liquids are described as 'fire resistant'. Of these, some, such as chlorinated paraffins and phosphate esters, are intrinsically fire resistant, but others, such as liquids dosed with antioxidant or hydraulic fluids containing water, are not, and may become combustible again if they suffer preferential loss of the antioxidant or water, respectively, in the warm lagging.

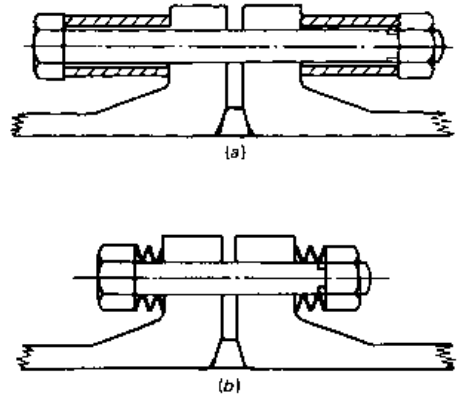


Figure 16.74 *Modification of existing joints (after McFarland, 1969): (a) use of longer bolts and sleeves; (b) use of Belleville washers (Courtesy of the American Institute of Chemical Engineers)*

The amount of oil which gives the maximum ignition sensitivity in the more porous insulating media is estimated by Gugan (1974a) as about 6–12% v/v (equivalent to about 150–300% w/w).

A continuous leak is not necessarily the most favourable to self-heating. If a suitable concentration of oil can only be maintained by a continuous flow, the oil is too volatile; and if there is a continuous flow of involatile oil, it is likely to oversaturate the lagging. Typical leakage points which may cause a lagging fire are pumps, flanged joints, and sample and drain points.

The material of insulation is another factor in determining self-heating, although it is generally less important than the nature of the oil. A good insulating material has a low thermal conductivity based on a porous structure of low density. It is precisely these features which favour self-heating. The important aspects for self-heating are the extent to which the material provides surface area on which the oil is exposed, allows air to diffuse in and prevents heat from being conducted away.

The insulation material may have some inhibiting or catalytic effect on self-heating in some systems. Bowes (1974a) quotes a difference in the minimum pipe temperature of 24°C for the ignition of oil in two different lagging materials.

Frequently the main insulating material is covered with an impervious cement finish or sealing material. This greatly reduces the extent to which oxygen can diffuse into the insulation.

The temperature which can be attained in the lagging depends on its geometry and on the pipe temperature. In some cases it is possible to estimate the lagging temperature resulting from self-heating by using theoretical methods in combination with suitable experimental tests, as described in Section 16.6.

There are a number of precautions which can be taken against lagging fires. One is to prevent the lagging becoming soaked with oil. This means primarily a high standard of operation and maintenance to avoid leaks. But, in addition, measures may be adopted such as not lagging flanged joints and protecting lagging at sample points with sheet metal collars.

As discussed earlier, the maximum temperature which is attained in self-heating depends on the thickness of the lagging. A thick lagging gives good heat insulation, but also favours self-heating. A compromise is necessary, therefore, between these two factors.

Methods of making the lagging surface impervious to air include the use of a cement finish, bituminous coating material or aluminium foil. If such sealing is used, it is necessary to ensure that the sealing is maintained, particularly at the ends of the lagging.

Another approach is to use not the usual type of insulating material but other insulation such as foam glass or crimped aluminium sheeting. Foam glass is relatively brittle and requires additional care. It is more expensive, although the price differential appears to be narrowing. Aluminium sheeting is another alternative, although it is not a particularly good insulation. It has been suggested that the use of aluminium introduces the hazard of aluminium–iron smear ignition.

On some plants with high risk and difficult self-heating problems, the approach adopted is to do without insulation altogether. In such cases expanded metal 'stand-offs' may be used to protect personnel from the hot pipework.

A lagging fire is usually detected by the evolution of smoke or other fumes. Such fumes are in fact the most satisfactory means of detection insofar as they precede incandescence as well as accompany it. It is usually a matter of chance, however, whether self-heating is detected before a fire has developed.

The use of temperature sensitive paints has been suggested as a means of detection, but this is not likely to be particularly effective since the lagging surface temperature is not a very reliable indicator of self-heating.

The hazard from a lagging fire may be that of flames issuing from the lagging. But frequently the worst hazard occurs when the lagging is opened up to remove the smouldering material. The fire may then grow, sometimes very strongly, particularly if it has been deprived of air previously.

Flames from a lagging fire should normally be extinguished with small quantities of water. Water should also be available to extinguish fire when smouldering lagging is removed. Fire extinguishing agents which do not contain water are generally less effective, because of the high risk of re-ignition. Regard should be paid, however, to any hazard which the use of water may involve, such as that associated with electrical equipment. Any lagging which might re-ignite should be removed to a safe place. Further precautions may be required if the lagging contains asbestos material or evolves toxic fumes.

Accidents involving lagging fires are described in Case Histories A115 and A122.

16.11.4 Duct and cable fires

Ducts of various kinds are common in process plants and buildings. They include ducts used for (1) the conveyance of fluids, (2) extraction and other ventilation, (3) pipes and (4) electrical cables.

Such ducts may have walls which are combustible and/or may contain combustible materials. In ordinary ventilation systems the duct walls may be plastic. In fume extraction systems combustible deposits may build up on the duct walls. Cable and pipe coverings may be combustible. Other sources of combustible material include leaks from pipes and debris left in the duct.

In many ducts air flow occurs due to forced ventilation, which is used not only in the ventilation and extraction systems, but also to dilute leaks in ducts carrying pipes. In other cases air flow may occur in fire conditions due to the flue effect.

If combustible material in a duct is ignited, fire growth can be rapid, because the heat does not escape as readily as in an open fire and much of it serves to preheat surfaces further down the duct, making the fire much more severe and causing combustion of materials which would not normally make much contribution to a fire.

Accounts of duct fires include those by A.F. Roberts (1969/70) and Anon. (1979 LPB 30, p. 155). Investigations have been carried out by Roberts and co-workers (A.F. Roberts and Clough, 1967a,b; A.F. Roberts, 1969/70, 1971a). These have included experimental work on fires in ducts with walls of wood and of polyurethane.

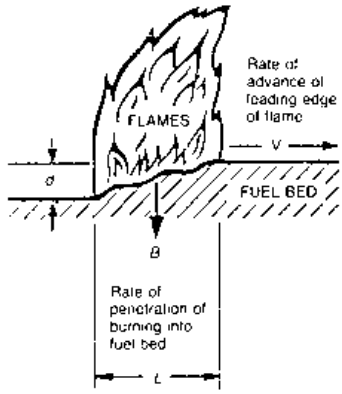


Figure 16.75 *Flame spread in a duct fire (A.F. Roberts, 1969/70) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

Roberts has given a model of duct fires in which, as shown in Figure 16.75, important parameters are the length L of the flame zone and the velocity V of the advance of the leading edge of the flame. From these the dimensionless parameters L^* and V^* may be defined as

$$L^* = \frac{4CfLB\rho_f}{V_A \rho_A D} \qquad [16.11.1]$$

$$V^* = \frac{4CfVd\rho_f}{V_A \rho_A D} \qquad [16.11.2]$$

where B is the rate of penetration of burning into the fuel bed, C is the mass of air required for the complete combustion of unit mass of fuel, d is the depth of fuel bed consumed by the fire, D is the duct diameter, f is the fraction of surface covered by the lining, V_A is the velocity of the air, ρ_A is the density of the air and ρ_f is the density of the fuel bed.

An important distinction is between oxygen-rich and fuel-rich fires. The parameter L^* is effectively a fuel/air ratio so that the conditions for such fires are that for $L^*<1$ the fire is oxygen rich, while for $L^*>1$ it is fuel rich.

A fuel rich fire is the more serious hazard. There is a greater rate of flame advance and heat release, the combustion gases still contain a large proportion of flammable material and they are also toxic. In a fuel rich fire the flame advances some 10 times as rapidly as in an oxygen rich fire. Potentially combustible materials are subject to prolonged preheating by flames and combustion products at 1000–1300°C. At a fuel/air ratio of 3, two-thirds of the material vaporized or pyrolysed is still unreacted. The combustion gases contain a large proportion of carbon monoxide. Evidence indicates that fuel rich combustion is favoured by narrow ducts, high air velocities, high fuel loading, the presence of obstructions and large ignition sources.

In an established duct fire, the transition from oxygen rich to fuel rich conditions tends to increase the hazard. Reduction of the air flow may thus actually make things worse. Since the combustion gases leaving the duct may still be highly flammable, they present the hazard of further fire and explosion. These gases also contain large amounts of smoke and toxic gas, which are not only hazardous, but also tend to hamper severely attempts to fight the fire.

Work by C.K. Lee, Chaiken and Singer (1979) on duct fires with forced ventilation indicates that the fire can cause an appreciable increase in the flow resistance of the duct and can even lead to flow reversal.

Much of the interest in duct fires relates to fire in coal mine roadways, where wood is used as a lining. Work on such fires has been done by Roberts and co-workers (A.F. Roberts and Kennedy, 1965; A.F. Roberts, Clough and Blackwell, 1966; A.F. Roberts and Clough, 1967a,b) and by de Ris (de Ris, 1970; A.F. Roberts, 1971a).

These studies indicate that in modelling duct fires with infinitely thick walls there is need for care in making the assumption of a steady state. Roberts comments that a fully developed duct fire would be a highly elongated phenomenon and suggests that the full length of the fire, from the start of the burnt out zone to the end of the preheating zone, might be of the order of 370 times the duct diameter.

Another point highlighted by this work is the uncertainty surrounding the value of the heat of vaporization H_{vap} of wood, which extends not only to the magnitude but even to the sign.

There are a number of precautions which may be taken against duct fires. Good housekeeping can reduce the amount of combustible material in the duct. Fire detectors may be provided to give early warning. Fire stops may be installed to prevent fire spread. The duct may be designed to allow access for fire fighting. Fire protection systems of various kinds are available. Proper working practices may be enforced by the use of a permit-to-work system.

As stated earlier, a case history of a duct fire is given by Anon. (1979 LPB 30, p. 155). Other case histories include those of cable tray fires as described below.

A type of duct fire which is of particular concern in process plants is cable tray fires. This problem has been discussed by the FPA (1974a) and by Anon. (1980 LPB 41, p.5). This is an important matter, because damage to cable systems often results in a long outage.

The widespread use of electric motors in process plants has led to a proliferation of motor control centres and large electric power and control cable runs. In a large proportion of cases it is not practical to use metal conduits and cables are run in open metal troughs.

A single cable may not burn very readily, but a number of cables will often burn vigorously, particularly in a vertical duct which is favourable to fire spread. Once heated up cables may not need a flame to ignite them. Rubber covered cables can be ignited by hot air or radiant heat.

PVC insulated cables present a particular problem. They burn well and readily spread fire in vertical ducts, with the plastic melting and releasing burning droplets. The PVC also decomposes to give large quantities of hydrogen chloride gas which is toxic and renders corrosive the water used in fire fighting. In one power station fire about a third of the damage was attributed to this cause.

Where power and control cables are mixed, short circuits can occur from high current lines to lines which are not rated for such currents.

Cable ducts form a means by which fire may spread. This is especially serious where the cable ducts lead to a vulnerable point such as a control room.

Ignition in several cable fires has been assisted by an oil leak from machinery which has entered the cable duct through an unsealed opening.

Damage to cables may disable the emergency system, including the telephones required to summon assistance. In one incident notification of the fire brigade was delayed because the telephone circuits had failed.

There are a number of precautions which may be taken against cable fires. Cables may be segregated from other services and the different types of cable, particularly power and instrument cables, may be segregated. The criticality of all cable runs should be assessed and an appropriate degree of protection provided for each. The hazard of fire spread through cable ducts to vulnerable points should be minimized.

Fire protection for petrochemical plants and oil platforms has been discussed by Corona (1984) who states that a fire protection system for cabling should be based on a hydrocarbon pool fire at not less than 1800°F (980°C), should maintain the cable temperature within operating limits, which on ordinary PVC cables is usually below 300°F (149°C), and should do this for a time period long enough for emergency operation of equipment, which might be of the order of 20 minutes. Another time period often quoted for cable protection in petrochemical plants is 15 minutes.

Use may be made of fire resistant cabling. If reliance is placed on such fire resistance, it is important to select the right cable. This is partly a matter of specifying the degree of fire resistance required and partly one of assessing whether a given cable meets this specification. Several workers have emphasized that any tests conducted should be on a sufficiently large scale as to be realistic.

The problem of fire testing of cables and of standard fires for such tests is discussed by Schultz (1986). He describes the protection of cables using a ceramic-refractory blanket held by steel bands.

Spillage of oil into the cable duct may be minimized by sealing the cable holes. Protection against the spread of fire through the duct may be provided by fire stops. The design of such stops is discussed by Anon. (1980 LPB 41, p. 5).

Smoke detection devices may be used to give early warning. The cable duct may be designed to give access for fire fighting with a maximum distance between access points. Points may be provided to receive high expansion foam from mobile generators.

Use is also made of sprinklers and other fixed fire protection systems. The application of such protection to electrical cables is a specialist matter.

Protection against cable fires is required during construction as well as during operation. There have been several serious cable fires during the construction phase.

Accounts of case histories of cable fires have been given by the FPA (1974a) and by Anon. (1980 LPB 41, p. 5).

16.11.5 Storage tank fires

Storage tank fires are not infrequent in process plant and other sites. The quantities of material involved, and consequently the losses, tend to be large. The problem is discussed in *Fire Protection Manual for Hydrocarbon Processing Plants* (Vervalin, 1964a, 1973a), in *Tank Fires* (OIA, 1974 Loss Inf. Bull. 400–1) and by a number of other authors (e.g. Burgoyne, 1950; Kletz, 1971).

Storage is discussed in Chapter 22, where the main types of storage tank are described. The larger storage tanks are atmospheric tanks of the fixed roof or floating roof types. The main materials held in atmospheric storage tanks are flammable liquids.

The scale of the fire/explosion on a storage tank installation can be very large. A single 'jumbo' storage tank in the petroleum industry may have a capacity of 500 000 barrels or more. In many tank fires more than one tank is involved.

The frequency of fires/explosions in fixed roof tanks containing volatile hydrocarbons has been estimated by Kletz (1971) as once in 833 tank-years. The estimated frequency for tanks holding non-hydrocarbons is one-tenth of this value. Comparable data for floating roof tanks are not given.

It is also apparent that, in addition to accidents involving fire/explosion, there are also near misses in which, for example, tanks are buckled but do not rupture.

In some cases there is a fire/explosion of a flammable mixture in the vapour space of the tank. In others a vapour cloud forms outside the tank and the ignites. Other cases are fire following liquid slopover or liquid spillage due to tank rupture.

One of the most frequent causes of tank fires/explosions is overfilling of the tank. This is usually due to defects in operating procedures, failure of instrumentation and/or operator error. Failure of ancillary equipment, such as pumps, and strikes of lightning are other common causes.

If there is an initial explosion which blows the tank roof off, a fire may be established in the tank and may burn there without spreading.

If there is a spillage of liquid into the bund around the tank, due to overfilling, a vapour cloud may form, find a source of ignition, and flash back. This may ignite the liquid leaving the tank and/or that in the bund.

If there is a spillage of liquid in the bund from ancillary equipment, such as a pump, and the spillage again ignites, a general fire may occur. Initially at least there may be no fire in the tank.

Once a fire is established, it frequently causes failures which feed the fire. Thus a fire on equipment such as pumps or pipework within the bund can cause a pipe failure which then results in spillage of the tank contents into the bund. Experience shows that pipework exposed to a strong fire in a bund usually fails within about 10–15 minutes, and heat radiation from a tank fire may cause other nearby tanks to fail.

There are a number of measures which can be taken to reduce the risk of tank fires. Much can be done by good plant layout. There should be generous spacing between tanks to reduce the risk from radiant heat. Tanks should be provided with water spray systems which drench them in water and keep them cool. To

some extent there is a trade-off which can be made between these two measures.

Frequently the fire engulfs all tanks in the bund. It is highly desirable, therefore to have a separate bund for each tank, particularly for large tanks.

Pipework inside bunds should be kept to a minimum with as few flanges, valves and other fittings as possible. Pipework can be buried, but then tends to corrode. Pumps should be installed outside bunds, both because they are sources of leakage and of ignition, and because they are often needed to fight the fire by pumping out the tank.

Measures should be taken to prevent overfilling of the tank. A high level alarm is normally a minimum requirement and often a high level trip is desirable. This instrumentation should be backed up by appropriate operating procedures.

If a fire occurs in a tank, the water sprays should be activated to protect the other nearby tanks. It is often appropriate to pump down to a suitable receiver the tank which is on fire, but it should be borne in mind that in the later stages of this operation the liquid may be very hot and may create a hazard at the receiver.

Tank fires are fought with water and/or foam. The quantities required are very large. It is essential, therefore, that the fire water mains be adequately sized, both for the fire pumps and for the drench water sprays. The tank farm should not be a backwater in this respect. Similarly, there should be a substantial storage of foam.

A tank fire can be difficult to fight for several reasons. The conditions favour the formation of vapour clouds. Metal surfaces become and remain very hot. In consequence, there is frequently flashback of fire to an area where it had appeared to have been extinguished.

Some atmospheric storage tanks contain refrigerated liquefied flammable gas. There is much less experience, however, with fires on such tanks.

Liquefied flammable gases are also stored in pressure vessels. Again, at a pressure storage vessel overfilling is one of the most frequent causes of fire. A fire which develops around a storage vessel containing a liquid under pressure can cause the pressure in the vessel to build up so that there is an explosion.

It is normal practice to provide a pressure relief valve on such vessels and it is essential for it to be properly designed and maintained, although this does not fully protect against the hazard. If the vessel is overheated, it may rupture even though the relief valve has operated. The occurrence of boiling liquid expanding vapour explosions (BLEVEs) on pressure storage vessels is described in Chapter 17.

Measures should be taken to minimize fire and explosion on pressure storage vessels. The ground underneath the vessel should be sloped away to prevent accumulation of flammable liquid. There should be water sprays and/or fireproof thermal insulation to give protection against fire exposure and there should be safeguards against overfilling.

16.11.6 Major fire events

In addition to the various types of process plant fire just described, there are a number of major fire events to which process plants are vulnerable. These are (1) vapour cloud fires, (2) fireballs, (3) pool fires, (4) jet flames and (5) engulfing fires. These are described in Sections 16.14, 16.15, 16.17, 16.19 and 16.20, respectively.

16.11.7 CCPS *Fire and Explosion Model Guidelines*

Guidance on the modelling of such major fire events is given in the CCPS *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires and BLEVEs* (1994/15) (the CCPS *Fire and Explosion Model Guidelines*).

The *Guidelines* deal with (1) vapour cloud, or flash, fires, (2), vapour cloud explosions and (3) BLEVEs. They also cover (4) fireballs, which are treated as an aspect of BLEVEs. For each of the three phenomena the *Guidelines* outline basic physical concepts, experimental work and available models and correlations for the phenomena themselves and for damage and injury, and give sample problems. They also contain a set of case histories.

Vapour cloud fires and fireballs are treated here in Sections 16.14 and 16.15, respectively and vapour cloud explosions and BLEVEs are discussed in Chapter 17.

16.12 Flames

An important factor in the consideration of both the causes and the effects of fires/explosions in process plants is the behaviour of flames. The study of combustion and flames is a specialist matter and only a few selected features are mentioned here. It is emphasized, however, that this discipline makes a very large contribution to loss prevention.

Accounts of combustion and flames are given in *Flames* (Gaydon and Wolfhard,1953–) and *Combustion, Flames and Explosion of Gases* (B. Lewis and von Elbe, 1961), in the other texts quoted in Section 16.3 and in the series *International Symposia on Combustion* (Combustion Institute, 1928–).

Certain aspects of the behaviour of flames inside plant have already been considered. These include flames in vessels, flames in pipes and cool flames, which were discussed in Section 16.3. The present section is concerned with flames in the open.

Flames outside the plant include those of:

(1) flash fires;
(2) pool fires;
(3) fireballs;
(4) flares;
(5) jet flames;
(6) fire engulfed vessels.

These are considered in the following sections.

In general, a complete model of a flame will include information on:

(1) flame shape and dimensions;
(2) heat release rate;
(3) fraction of heat radiated;
(4) flame temperature;
(5) flame emissivity;
(6) surface emissive power;
(7) view factor.

However, it is often not necessary to have full information on all of these. If the flame can be treated as a point source, it may be characterized by the heat release rate

and the fraction of heat radiated and the simple point source view factor used. The other methods require the flame dimensions and may utilize a more accurate view factor. There are three approaches. One is to use the flame dimensions in combination with the heat release rate and the fraction of heat radiated, which together, in effect, give the surface emission. Another is to use the flame dimensions in combination with the flame temperature and flame emissivity, which together again give the surface emission. The third is to use the flame dimensions and the surface emissive power.

16.13 Radiant Heat Transfer

In many process plant fires the dominant mode of heat transfer is radiation. An account is given here of radiant heat transfer relevant in the present context, but it is emphasized that this is no more than an outline treatment of a rather complex topic. Standard texts on radiant heat transfer include *Radiation Heat Transfer* (Sparrow and Cess, 1966, 1978), *Thermal Radiation Heat Transfer* (Siegel and Howell, 1991) and *Radiative Heat Transfer* (Modest, 1993), and, for process plant, *Heat Transmission* (McAdams, 1954) and *Process Heat Transfer* (D.Q. Kern, 1950).

16.13.1 Thermal radiation

Radiant energy may be conceived as being transmitted either as electromagnetic waves or as photons. It travels at the speed of light and may be characterized either by its frequency ν or by its wavelength λ, which are related by the equation

$$c = \lambda\nu \qquad [16.13.1]$$

with

$$c = c_o/n \qquad [16.13.2]$$

where c is the velocity of light, n is the refractive index and the subscript o refers to vacuum conditions.

The electromagnetic spectrum ranges from γ-rays (wavelength $\approx 10^{-12}$ m) to radio waves (wavelength ≈ 10–10^2 m). The range of wavelengths for thermal radiation is approximately 0.3–50 μm. As shown in Figure 16.76, this range spans the infrared and visible ranges and part of the ultraviolet range.

16.13.2 Black body radiation

It has been shown by Planck from thermodynamic considerations that there is a maximum amount of radiant energy of a given frequency which can be emitted at a given temperature. An object which emits this quantity is termed a black body and the quantity itself the monochromatic, or spectral, emissive power for black body radiation. The fundamental form of Planck's law is

$$e_{b\nu} = \frac{2\pi h\nu^3 n^2}{c_o^2[\exp(h\nu/kT) - 1]} \qquad [16.13.3]$$

where $e_{b\nu}$ is the monochromatic emissive power for a black body, h is Planck's constant and k is Boltzmann's constant.

On the assumption that the refractive index is independent of frequency

$$\nu = c_o/n\lambda \qquad [16.13.4]$$

Equation 16.13.3 may be reformulated in terms of the wavelength λ using the relation

$$e_{b\nu}\,d\nu = -e_{b\lambda}\,d\lambda \qquad [16.13.5]$$

which yields the equation

$$e_{b\lambda} = \frac{2\pi hc_o^2}{n^2\lambda^5[\exp(hc_o/n\lambda kT) - 1]} \qquad [16.13.6]$$

or

$$e_{b\lambda} = \frac{c_1}{n^2\lambda^5[\exp(c_2/n\lambda T) - 1]} \qquad [16.13.7]$$

with

$$c_1 = 2\pi hc_o^2 \qquad [16.13.8a]$$

$$c_2 = hc_o/k \qquad [16.13.8b]$$

Equation 16.13.7 may be further recast in the form

$$\frac{e_{b\lambda}}{\sigma n^3 T^5} = \frac{c_1/\sigma}{(n\lambda T)^5[\exp(c_2/n\lambda T) - 1]} \qquad [16.13.9]$$

where σ is the Stefan–Boltzmann constant. The quantity on the right-hand side of Equation 16.13.9 is a function solely of $n\lambda T$. The form of this function is shown in Figure 16.77.

The principal black body radiation constants are:

Speed of light in vacuum $c_o = 2.9979 \times 10^8$ m/s
Planck's constant $h = 6.626 \times 10^{-34}$ J s
Boltzmann's constant $k = 1.381 \times 10^{-23}$ J/K
Stefan–Boltzmann constant $\sigma = 5.6705 \times 10^{-8}$ W/m^2 K^4
First radiation constant $c_1 = 3.742 \times 10^{-16}$ W m^2
Second radiation constant $c_2 = 0.01439$ m K

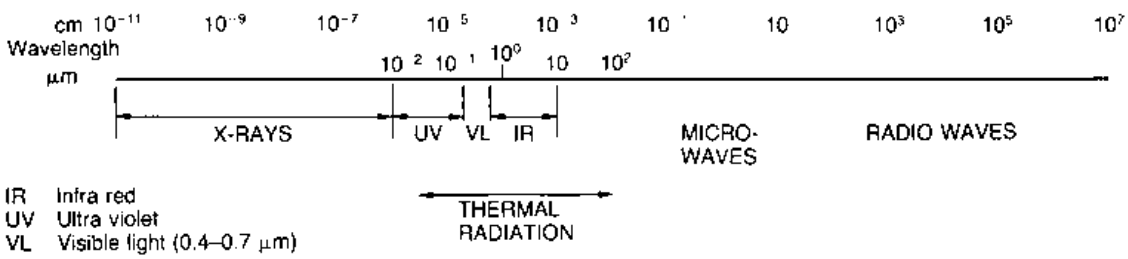


Figure 16.76 *The electromagnetic spectrum*

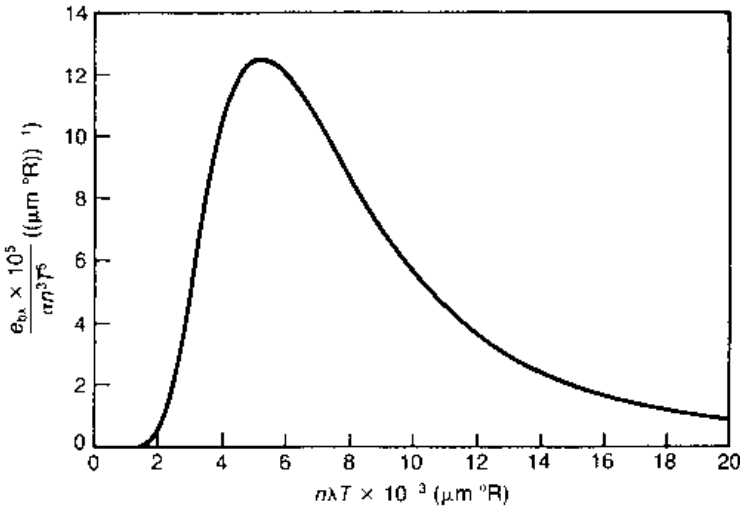


Figure 16.77 *Emissive power of a black body (Sparrow and Cess, 1978) (Courtesy of Brooks/Cole Publishers)*

The total emissive power of a black body is thus

$$e_b = \int_0^\infty e_{b\nu}\, d\nu \qquad [16.13.10]$$

Then from Equation 16.13.3

$$e_b = n^2 \frac{(2\pi k^4)T^4}{c_o^2 h^3} \int_0^\infty \frac{x^3}{e^x - 1}\, dx \qquad [16.13.11]$$

$$= n^2 \frac{(2\pi k^4)T^4}{c_o^2 h^3} \frac{\pi}{15} \qquad [16.13.12]$$

$$= n^2 \sigma T^4 \qquad [16.13.13]$$

Equation 16.13.13 is the Stefan–Boltzmann equation.

The refractive index n in Equation 16.13.13 is conventionally taken as unity. This is the value in most practical applications involving transmission of radiation through a gas. The equation than reduces to

$$e_b = \sigma T^4 \qquad [16.13.14]$$

16.13.3 Non-black and gray body radiation

For a non-black body the monochromatic emissive power e_λ is

$$e_\lambda = \epsilon_\lambda e_{b\lambda} \qquad [16.13.15]$$

where ϵ_λ is the monochromatic hemispherical emissivity.

It is also necessary to consider the absorption of radiation. If radiation incident on the surface is H_λ, the amount absorbed is $\alpha_\lambda H_\lambda$ and that reflected is $\rho_\lambda H_\lambda$, where α_λ is the monochromatic hemispherical absorptivity and ρ_λ the monochromatic hemispherical reflectivity. For an opaque surface

$$\alpha_\lambda + \rho_\lambda = 1 \qquad [16.13.16]$$

It has been shown that for a system in thermodynamic equilibrium that

$$\epsilon_\lambda = \alpha_\lambda \qquad [16.13.17]$$

Equation 16.13.17 is Kirchhoff's law.

For a black body ϵ_λ is unity and so therefore is α_λ. Thus a black body is also a perfect absorber as well as a perfect emitter of radiation.

The total emissive power e of a non-black body is

$$e = \int_0^\infty e_\lambda\, d\lambda \qquad [16.13.18a]$$

$$= \int_0^\infty \epsilon_\lambda e_{b\lambda}\, d\lambda \qquad [16.13.18b]$$

The overall emissivity ϵ is

$$\epsilon = e/e_b \qquad [16.13.19]$$

$$= \frac{\int_0^\infty \epsilon_\lambda e_{b\lambda}\, d\lambda}{\int_0^\infty e_{b\lambda}\, d\lambda} \qquad [16.13.20]$$

$$\alpha = \frac{\int_0^\infty \alpha_\lambda H_\lambda\, d\lambda}{\int_0^\infty H_\lambda\, d\lambda} \qquad [16.13.21]$$

where H_λ is the hemispherically incident radiation per unit area per unit time.

The emissivity ϵ is a function of the surface. The absorptivity α, on the other hand, is a function not only of the surface but also of the nature of the incident radiation.

There are several cases for which a simple relation between ϵ and α applies. The most important of these is the gray body. For a gray body ϵ_λ and α_λ are independent of wavelength λ and hence

$$\epsilon_\lambda = \epsilon \quad [16.13.22]$$

$$\alpha_\lambda = \alpha \quad [16.13.23]$$

Then from Kirchhoff's law as given in Equation 16.13.17

$$\alpha = \epsilon \quad [16.13.24]$$

In engineering applications the gray body assumption is frequently made.

Other cases where a simple relation holds between ϵ and α are described by Sparrow and Cess (1966, 1978).

For gray body radiation from an opaque material

$$\alpha + \rho = 1 \quad [16.13.25]$$

From Equations 16.13.14 and 16.13.19 the emissive power of a gray body is

$$\mathrm{e} = \epsilon\sigma T^4 \quad [16.13.26]$$

The total radiation from a gray body is given by the radiosity B, which is the sum of the radiation emitted by the surface and that reflected from it

$$B = \epsilon\sigma T^4 + \rho H \quad [16.13.27]$$

Radiation from a surface may be uniform in all directions or it may be directional. The two situations are termed diffuse and specular radiation, respectively. Surfaces of interest in engineering applications usually approximate to diffuse surfaces and the assumption is usually made that the radiation is diffuse.

In general, a surface tends to be diffuse at short wavelengths and specular at long wavelengths. Roughness increases the diffuseness of the surface.

16.13.4 Participating media

The radiation transmitted may be affected by the medium through which it passes. Radiation can suffer attenuation due to absorption and scattering. A medium which causes such attenuation is termed a participating medium.

Most monatomic and diatomic gases are non-participating media, except when at high temperature and/or when dissociated. Dry air is therefore also effectively a non-participating medium, but air containing water and air or gas containing water and carbon dioxide are participating media.

The attenuation of the radiation with distance x may be expressed by the relation

$$I_\lambda = I_{o\lambda} \exp(-\beta_\lambda x) \quad [16.13.28]$$

with

$$\beta_\lambda = \kappa_\lambda + \gamma_\lambda \quad [16.13.29]$$

where I_λ is the monochromatic radiation intensity, $I_{o\lambda}$ is the initial monochromatic radiation intensity, β_λ is the monochromatic extinction coefficient, κ_λ is the monochromatic absorption coefficient and γ_λ is the monochromatic scattering coefficient.

An overall absorption coefficient κ may be defined by the relation

$$\kappa = \frac{\int_0^\infty \kappa_\lambda \int_{4\pi} I_\lambda \, \mathrm{d}\omega \, \mathrm{d}\lambda}{\int_{4\pi} I \, \mathrm{d}\omega} \quad [16.13.30]$$

and a similar relation applies for the overall scattering coefficient γ.

16.13.5 Radiant exchange

The intensity of radiation i from a radiation source, as shown in Figure 16.78, is

$$i = \frac{\mathrm{d}\Phi}{\mathrm{d}\omega \cos\theta} \quad [16.13.31]$$

where Φ is the radiant flux contained within the solid angle $\mathrm{d}\omega$ and θ is the angle between the direction of this flux and the normal. For uniform, or diffuse, radiation

$$i = \Phi/\pi \quad [16.13.32]$$

A similar expression applies for radiosity

$$i = B/\pi \quad [16.13.33]$$

For the general situation of an arbitrary configuration with radiant transfer between two differential surfaces $\mathrm{d}A_i$ and $\mathrm{d}A_j$, as shown in Figure 16.79, the treatment is as follows. Noting that r is the distance between the surfaces and that $\mathrm{d}\omega$ is the solid angle subtended by $\mathrm{d}A_j$ when viewed from dA_i and that it is given by

$$\mathrm{d}\omega = \mathrm{d}A_j \cos\beta_j / r^2 \quad [16.13.34]$$

and that from Equation 16.13.33

$$i_i = B_i/\pi \quad [16.13.35]$$

the radiation leaving $\mathrm{d}A_i$ in the direction of $\mathrm{d}A_j$ may be expressed as

$$= i_i \, \mathrm{d}A_i \cos\beta_i \, \mathrm{d}\omega \quad [16.13.36]$$

or as

$$= B_i \cos\beta_i \cos\beta_j \, \mathrm{d}A_i \, \mathrm{d}A_j / \pi r^2 \quad [16.13.37]$$

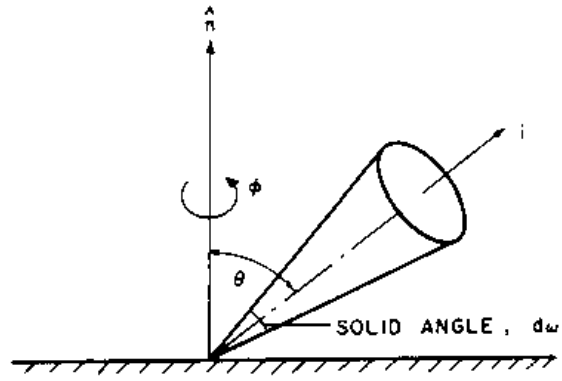


Figure 16.78 *Intensity of radiation (Sparrow and Cess, 1978) (Courtesy of Brooks/Cole Publishers)*

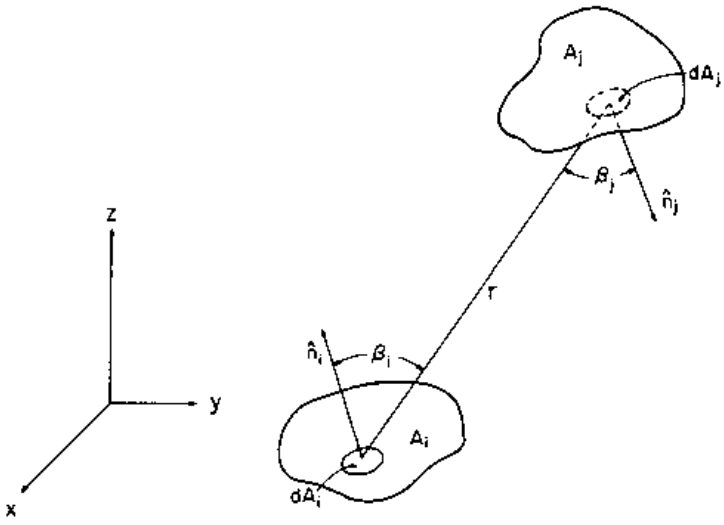


Figure 16.79 *Radiant interchange between two differential surfaces (Sparrow and Cess, 1978) (Courtesy of Brooks/Cole Publishers)*

An angle factor $dF_{dA_i-dA_j}$ may be defined as the fraction of the radiation $B_i\,dA_i$ which is incident on dA_j. Then

$$dF_{dA_i-dA_j} = \cos\beta_i \cos\beta_j\, dA_j/\pi r^2 \qquad [16.13.38]$$

Similarly, an angle factor $F_{A_i-A_2}$ may be defined for the radiation from finite surface A_1 to finite surface A_2. Angle factors are discussed in greater detail below.

It should be noted that such angle factors only take account of radiation from a source to a target and not of radiation back from the target to the source. In the applications of interest here, however, the latter is usually negligible.

Where it is necessary to consider radiation back from the target, an emissivity factor F_ϵ may be introduced. Then the product of the angle factor F_A and the emissivity factor F_ϵ is the overall interchange factor F_o

$$F_o = F_A F_\epsilon \qquad [16.13.39]$$

The application of these factors is described below.

There are a number of configurations which occur in engineering and for which simple solutions of the radiant flux are available. One is the case where a body with arbitrary radiation properties and at temperature T_1 is located inside a completely enclosed space with wall temperature T_2 such that black body radiation obtains. Then the net radiant heat transfer is

$$Q = A(\epsilon\sigma T_1^4 - \alpha\sigma T_2^4) \qquad [16.13.40]$$

For gray body conditions, Equation 16.13.40 reduces to

$$Q = A\epsilon\sigma(T_1^4 - T_2^4) \qquad [16.13.41]$$

Another case is where radiation occurs between black bodies consisting of two large parallel planes 1 and 2. For this case

$$Q = A\sigma(T_1^4 - T_2^4) \qquad [16.13.42]$$

For gray body conditions, following D.Q. Kern (1950), the radiant heat fluxes are

	Hot plane 1	*Cold plane 2*
Radiated	$e_1(=\epsilon_1\sigma T_1^4)$	$e_2(=\epsilon_2\sigma T_2^4)$
Returned	$e_1(1-\epsilon_2)$	$e_2(1-\epsilon_1)$
Radiated	$e_1(1-\epsilon_2)(1-\epsilon_1)$	$e_2(1-\epsilon_1)(1-\epsilon_2)$
Returned	$e_1(1-\epsilon_2)(1-\epsilon_1)$ $(1-\epsilon_2)$	$e_2(1-\epsilon_1)(1-\epsilon_2)$ $(1-\epsilon_1)$

Summation of these terms for the net radiant flux gives a series whose solution is

$$Q = A\frac{1}{(1/\epsilon_1)+(1/\epsilon_2)-1}\sigma(T_1^4 - T_2^4) \qquad [16.13.43]$$

which reduces to Equation 16.13.42 for $\epsilon_1 = \epsilon_2 = 1$.

Equations 16.13.41 and 16.13.43 may be reformulated in terms of the angle and emissivity factors to give

$$Q = AF_A F_\epsilon \sigma(T_1^4 - T_2^4) \qquad [16.13.44]$$

where for Equation 16.13.41 $F_A = 1$ and $F_\epsilon = \epsilon$, and for Equation 16.13.43 $F_A = 1$ and

$$F_\epsilon = \frac{1}{(1/\epsilon_1)+(1/\epsilon_2)-1} \qquad [16.13.45]$$

16.13.6 Heat radiation

The main application of radiant heat transfer in the present context is the estimation of the heat radiated from flames in accident conditions. Accounts of flame radiation are given in the standard texts on radiant heat transfer. A review relevant to process plant fires has been made by Considine (1984 SRD R297).

The radiant heat flux emitted by a flame in such a situation is given by the relation

$$E = \epsilon\sigma T^4 \qquad [16.13.46]$$

$$= \frac{Q_r}{A_f} \qquad [16.13.47]$$

with

$$Q_r = F_r Q_c \qquad [16.13.48]$$

where A_f is the surface area of the flame, E its surface emissive power, F_r the fraction of heat released which is radiated, Q_c the total heat released by combustion and Q_r the total heat radiated.

The heat received by the target is

$$I = \alpha\tau FE \qquad [16.13.49]$$

where F is the view factor, I the heat radiation intensity received by the target and τ is the atmospheric transmissivity.

These equations are used in conjunction with relations for the geometry of the flame and for the heat radiated per unit area of the flame surface.

There are alternative approaches to the estimation of the heat radiated Q_r. One is to work in terms of the flame temperature and emissivity. Another is to use empirical values of the surface emissivity of the flame envelope. A third is to calculate the total heat generated and to apply a factor F_r for the fraction of heat radiated.

16.13.7 Heat radiation: flame emissivity

If the first, and most fundamental, of these approaches is adopted, it is necessary to estimate the emissivity of the flame. The emissivity of a flame depends on the type of fuel and on the nature of the combustion. The heat radiated from a flame is emitted by gases, in particular the products of combustion CO_2, H_2O, N_2, CO and O_2 and by carbon particles, or soot. The former are band emitters while the latter emit over a continuous range. A flame in which the radiation is emitted solely from the gaseous constituents is termed non-luminous and one in which there is soot is termed luminous.

CO_2 and H_2O

The principal gaseous contributors to flame emissivity are carbon dioxide and water vapour. The emissivity ϵ_g of a non-luminous flame may be estimated from that of these gases using the relation

$$\epsilon_g = \epsilon_c + \epsilon_w - \Delta\epsilon \qquad [16.13.50]$$

where ϵ_c and ϵ_w are the emissivities of CO_2 and H_2O, respectively, and $\Delta\epsilon$ is a correction term which allows for the overlap between the bands for these two gases.

Flame emissivity is required for many furnace calculations and there is a standard method of estimating it. The method is as follows. The emissivity for each gas species is a function of the partial product path length

$$e_c = f(p_c L) \qquad [16.13.51a]$$

$$\epsilon_w = f(p_w L) \qquad [16.13.51b]$$

where L is the mean path length, p_c is the partial pressure of CO_2 and p_w is the partial pressure of H_2O.

In process calculations, it is necessary to make a correction to the partial pressure path length products for carbon dioxide and water if the total pressure is other than atmospheric. Plots for the correction factors C_c and C_w are given in standard texts. These corrections are not required for flames at atmospheric pressure, which are those of prime interest here. The mean beam length L is considered below.

The correction term $\Delta\epsilon$ is a function of the ratio of the partial pressure of water to the sum that of the two gases

$$\Delta\epsilon = f\left(\frac{p_w}{p_c + p_w}\right) \qquad [16.13.52]$$

Graphs for the determination of the two gas emissivities ϵ_w and ϵ_c and the correction $\Delta\epsilon$ given by Hottel (1954), from the experiments of Hottel and Mangelsdorf (1935) and Hottel and Smith (1935) for carbon dioxide and the correlation of Hottel and Egbert (1942) on water vapour, are shown in Figure 16.80.

Soot

An account of the properties of soot and of its occurrence in different types of flame is given by H.G. Wagner (1979). Soot usually forms in flames in the temperature range 1000–2500°C. The total amount of soot is only a small fraction of the carbon present. Theoretically, from the stoichiometry for a hydrocarbon, soot formation should start when the carbon/oxygen ratio (C/O) reaches unity, but in practice it starts around $C/O \approx 0.5$. In work on gaseous diffusion flames on burners it has been found that the soot concentration is a maximum along the axis, where measurements by Kunugi and Jinno (1967) gave concentrations of 3×10^8 particles/cm^3, or 10^{-7}–10^{-6} g/cm^3. In their classic work on turbulent diffusion flames, Dalzell, Williams and Hottel (1970) found axial concentrations of soot of 10^{-6} g/cm^3.

The characterization of the emissivity of soot is somewhat complex. The emissivity is a function of the wavelength, and the following expression has been suggested

$$\epsilon_{s\lambda} = k_1/\lambda^{k_2} \qquad [16.13.53]$$

where $\epsilon_{s\lambda}$ is the emissivity of soot at wavelength λ, and k_1 and k_2 are constants. The value of the constant k_2 is of the order of unity.

As described by Markstein (1974), highly sooty flames satisfy gray gas models. This implies that the radiation is concentrated in a relatively narrow waveband, which in turn indicates that the emitting soot particles are distributed over a narrow temperature range.

A relation widely quoted for the emissivity of soot from non-gray analysis is

$$\epsilon_s = 1 - \frac{15}{\pi^4}\psi^{(3)}(1 + X) \qquad [16.13.54]$$

with

$$X = \frac{cLT}{c_2} \qquad [16.13.55]$$

$$c = 36\pi f_v \frac{n^2 k}{[n^2 - (nk)^2 + 2]^2 + 4(nk)^2} \qquad [16.13.56]$$

where c is the effective soot concentration (volume fraction), f_v is the volume fraction of soot particles, L is the path length, T is the absolute temperature, X is a parameter and $\psi^{(3)}$ is the pentagamma function; c_2 is the

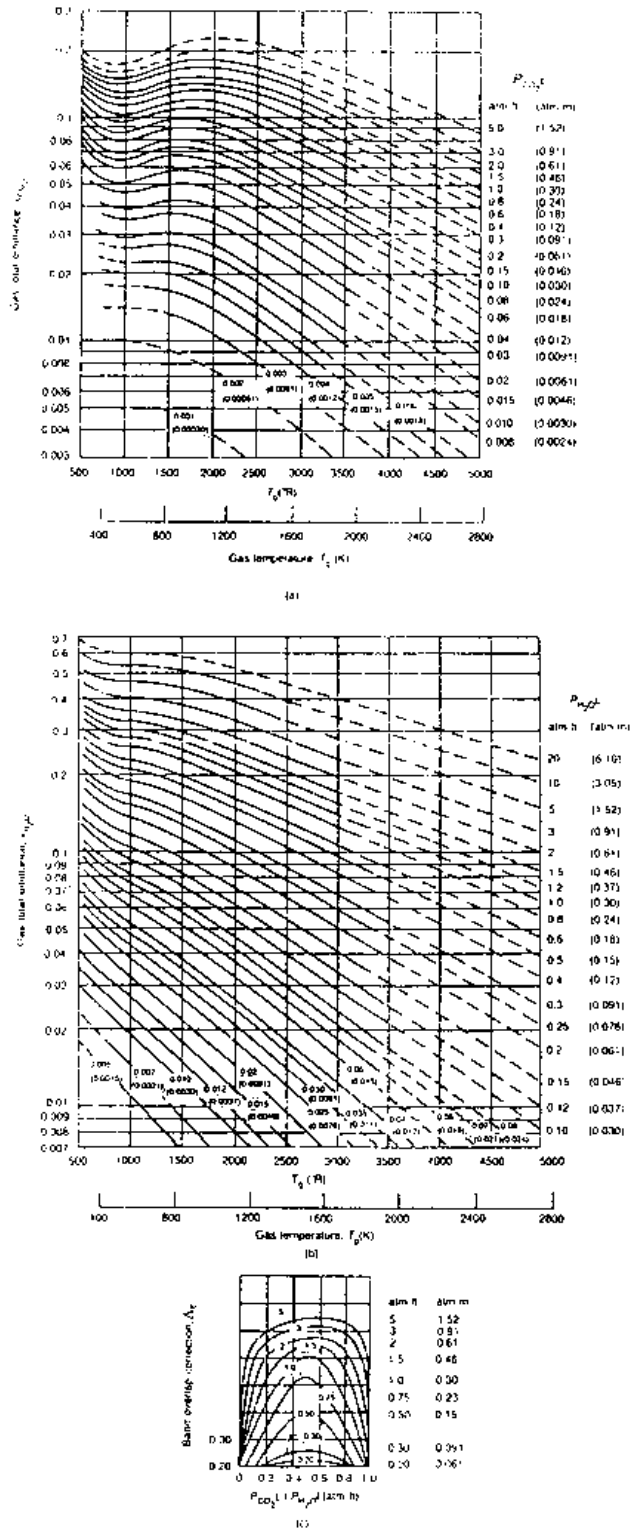


Figure 16.80 *Emissivity of carbon dioxide and water vapour (Siegel and Howell, 1991): (a) carbon dioxide; (b) water vapour; and (c) overlap correction term (Courtesy of Hemisphere Publishing Corporation)*

Planck second constant, and k and n are the infrared-average optical constants of soot particles. The penta-gamma function is given by Abramowitz and Stegun (1974).

It has been shown by Dalzell and Sarofim (1969) that an alternative, and more convenient, equation which gives results similar to Equation 16.13.54 is

$$\epsilon_s = 1 - \frac{1}{(1+Y)^4} \qquad [16.13.57]$$

with

$$Y = \frac{k_3 CLT}{c_2} \qquad [16.13.58]$$

where C is the volume fraction of soot particles, Y is a parameter and k_3 is a constant. The value of the constant k_3 is discussed by Siegel and Howell who use a value $k_3 = 5.0$ in some of their calculations.

A method for the emissivity of soot has been given by Yuen and Tien (1977) based on a gray analysis. They take

$$\epsilon_s = 1 - \exp(-\kappa L) \qquad [16.13.59]$$

with

$$\kappa = 3.6\frac{cT}{c_2} \qquad [16.13.60]$$

where T_m is the mean absolute temperature of the flame and κ is a parameter. The constant 3.6 is that required to ensure that Equation 16.13.59 yields results similar to those given by Equation 16.13.54.

These authors give a tabulation of values of these variables for a number of gaseous fuels, which includes:

Gas	*C/H*	c	κ (cm^{-1})	T_m (K)
Methane	0.25	2.00×10^{-5}	0.0645	1289
Ethane	0.33	1.60×10^{-5}	0.0639	1590
Propane	0.38	3.41×10^{-5}	0.1332	1561
n-Butane	0.40	3.12×10^{-5}	0.1259	1612
Ethylene	0.50	2.76×10^{-5}	0.1192	1722
Propylene	0.50	6.46×10^{-5}	0.2407	1490

Combined CO_2, H_2O and soot

For the emissivity ϵ_m of a gray gas containing CO_2, H_2O and soot, Yuen and Tien use the method just described for the emissivity ϵ_s of soot together with the relation

$$\epsilon_m = \epsilon_s + \epsilon_g(1 - \epsilon_s) \qquad [16.13.61]$$

A method for the estimation of the emissivity of a gray gas containing CO_2, H_2O and soot, i.e. a gas–soot mixture, has been described by P.B. Taylor and Foster (1974, 1975). These authors express the emissivity ϵ_m of such a mixture as

$$\epsilon_m = \sum_{n=1}^{3} a_{m,n}[1 - \exp(-K_{m,n}L)] \qquad [16.13.62]$$

with

$$K_{m,n} = \exp(q_{1,n} + q_{2,n}c) \qquad c > 0.0005 \qquad [16.13.63]$$

except that

$$K_{m,1} = 0.09 + 500c \qquad c \le 0.0005 \qquad [16.13.64]$$

and with

$$a_{m,n} = r_{1,n} + r_{2,n}T \qquad n = 1 \text{ or } 2 \qquad [16.13.65]$$

$$a_{m,n} = 1 - (a_{m,1} + a_{m,2}) \qquad n = 3 \qquad [16.13.66]$$

where c is the concentration of soot (kg/m^3), L is the path length (m) and T is the absolute temperature (K); $a_{m,n}$ is a weighting coefficient, $K_{m,n}$ is an absorption coefficient and $q_{1,n}$, $q_{2,n}$, $r_{1,n}$ and $r_{2,n}$ are coefficients; subscript m denotes a mixture and n denotes the component of the mixture.

These relations are applicable to the combustion of oil ($p_w/p_c = 1$) and gas ($p_w/p_c = 2$) at atmospheric pressure with $p_c = 0.1$ atm over the temperature range 1400–2400 K for path lengths between 0.01 and 10 m.

The values given for the coefficients are:

	$p_w/p_c = 1$		$p_w/p_c = 2$	
n	$q_{1,n}$	$q_{2,n}$	$q_{1,n}$	$q_{2,n}$
1	−1.252	558.55	−1.274	590.82
2	−0.221	665.38	−0.233	672.04
3	2.608	839.62	2.452	692.61

and

Soot concentration,	*n*	$p_w/p_c = 1$		$p_w/p_c = 2$	
c (kg/m^3)		$r_{1,n}$	$r_{2,n}$	$r_{1,n}$	$r_{2,n}$
0.0001	1	0.8119	−0.0000355	0.7191	−0.0000336
	2	0.0280	0.0001013	0.0804	0.0001131
0.0005	1	0.5478	−0.0001869	0.6123	−0.0002489
	2	0.3846	0.0002071	0.2688	0.0002901
0.001	1	0.5478	−0.0001869	0.6123	−0.0002489
	2	0.3846	0.0002071	0.2688	0.0002901

Further values are given by the authors.

Mean beam length

In his treatment of radiant heat transfer Hottel (1954) introduced the concept of the mean beam path length L, generally known as the mean beam length or path length, as a means of taking into account the geometry of the situation considered. He states: 'The mean beam length L may be thought of as the radius of a gas hemisphere which will radiate to unit area at the center of its base the same as the average radiation, over A, from the actual gas mass', where A is the area of interest.

A distinction, amplified below, is made between flames which are optically thick and those which are optically thin. If the flame is optically thin, and thus $p_g L \approx 0$, the corresponding mean beam length L_o is equal to four times the mean hydraulic radius

$$L_o = 4V/A \qquad [16.13.67]$$

where A is the area of the enclosure, L_o is the mean beam length for the optically thin condition, p_g is the partial pressure of the radiating gases and V is the volume of the enclosure.

Thus, for example, for a sphere

$$L_o = \frac{4\pi D^3/6}{\pi D^2} = \frac{2}{3}D \quad [16.13.68]$$

where D is the diameter of the sphere. For a long, thin cylinder

$$L_o = \frac{4\pi D^2/4}{\pi D} = D \quad [16.13.69]$$

where D is the diameter of the cylinder.

For a gas which is optically thick, Equation 16.13.67 is modified to give

$$L = C_{b1}L_o \quad [16.13.70]$$

where C_{bl} is a beam length correction factor. It is found that, as good approximation,

$$C_{b1} \approx 0.9 \quad [16.13.71]$$

Then from Equations 16.13.67, 16.13.70 and 16.13.71

$$L \approx 0.9\frac{4V}{A} \quad [16.13.72]$$

Following Hottel's original tabulation, values of the mean beam length L_o and of the beam length correction factor C_{bl}, more accurate than that of Equation 16.13.71, are listed for various geometries by Siegel and Howell (1991). Their results include:

System geometry	*Optical thickness tending to zero,* L_o	*Finite optical thickness,* L	*Correction factor,* C_{bl}
1. Sphere radiating to its surface	$2D/3$	$0.65D$	0.97
2. Cylinder with a height equal to twice its diameter radiating to the entire surface	$0.8D$	$0.73D$	0.91
3. Cube radiating to a face	$2X/3$	$0.6X$	0.90

where D is the diameter of the sphere or cylinder and X is the length of a side of the cube.

Optical thickness

Another aspect of effective flame emissivity is the extinction of radiation within the flame itself. The ratio of the heat radiated E to the heat radiated under black body conditions E_b is

$$\frac{E}{E_b} = 1 - \exp(-\beta L) \quad [16.13.73]$$

where β is an effective extinction coefficient and the subscript b denotes a black body. If the product βL is large, the flame is said to be optically thick and, conversely, if $\beta L \to 0$ the flame is said to be optically thin.

For a flame where the optical thickness depends only on the partial pressure p_g of the radiating gases, the condition for optical thinness may be stated as $p_g L \to 0$.

Hydrocarbon flames

The flames of some hydrocarbons, such as natural gas, contain relatively little soot, whereas those of other hydrocarbons, such as kerosene, contain much larger amounts. In consequence, with natural gas, for paths through the flame which in this context are short, say 5 m in length, the radiation exhibits a background level due to soot emission with superimposed peaks due to gaseous emission. As the path length increases so does the contribution of the soot, until at a path length of 10–20 m the emission spectrum becomes that of a black body.

Approximations

Frequently use is simply made of a point estimate of flame emissivity. A smoky flame is often assumed to be a black body radiator and thus to have an emissivity of unity. Values of emissivity of 0.9–1.0 are commonly used for such flames. LPG is a typical material which gives a smoky flame. LNG, on the other hand, tends to give a less smoky flame, but also a wider range of emissivities.

16.13.8 Heat radiation: fraction radiated

If the alternative approach is adopted of applying a radiant heat factor R, it is necessary to have appropriate values of this factor. Hymes (1983 SRD R275) has quoted the following values given by Roberts:

Type of flame	*Radiant heat factor*
Flare and jet flames	0.2
Pool fires	0.3
Fireballs from vessels bursting below relief valve pressure	0.3
Fireballs from vessels bursting above relief valve pressure	0.4

In general, the fraction of heat radiated depends on the efficiency of combustion and the soot formation and on the heat lost by convection to the entrained air. Some flame models include correlations in which the fraction of heat radiated is a function of the operating conditions.

Further discussion of flame emissivity, the radiant heat factor and the generalized heat flux is given in the sections below on specific types of flame.

16.13.9 Atmospheric transmissivity

As described above, appreciable attenuation may occur when radiation is transmitted from a source to a target through the atmosphere. Accounts of gas transmissivity have been given by D.Q. Kern (1950) and McAdams (1954). These are concerned primarily with radiant transfer in process plant items such as furnaces.

Treatments of atmospheric transmissivity have been given by Glasstone (1962) and Glasstone and Dolan (1980), Raj *et al.* (1979), Simpson (1984 SRD R304), V.C.

Marshall (1987), Wayne (1991) and the Committee for the Prevention of Disasters (CPD) (1992a). Other accounts of radiant heat transmission which include estimation of atmospheric transmissivity include those by R.O. Parker (1974), Lihou and Maund (1982) and Hymes (1983 SRD R275).

Attenuation of radiation in the atmosphere is due to absorption and scattering. The constituents of the atmosphere responsible for such attenuation are water vapour and carbon dioxide. Absorption of radiation is a function of the number of absorbing molecules in the path, while scattering is a function of the number and the size of the droplets.

Glasstone and Dolan (1980) state that, in general, the atmospheric transmissivity τ for estimation of the thermal radiation received by a target from a nuclear bomb explosion is a complex function which depends on the absorption, scattering and distance. For attenuation due only to absorption in a uniform atmosphere they give

$$\tau = \exp(-\kappa x) \qquad [16.13.74]$$

where x is the distance to the target and κ is the absorption coefficient. They also utilize this equation for the attenuation due to both absorption and scattering, but state that due to the latter, κ, now an attenuation coefficient, is then not constant with distance x.

They give the following relations between atmospheric condition and visibility:

Atmospheric condition	*Visibility* (km)
Exceptionally clear	280
Very clear	50
Clear	20
Light haze	10
Haze	4
Thin fog	2
Light to thick fog	≤ 1

and the following values relating the attenuation coefficient κ to the visibility:

Visibility (km)	κ (km^{-1})
80	0.03
40	0.1
20	0.2

A number of workers have utilized Equation 16.13.74 with suitable values of the attenuation coefficient. Lihou and Maund have used values ranging from $0.4\,km^{-1}$ for a clear day to $1.0\,km^{-1}$ for a hazy day with an average of $0.7\,km^{-1}$. Hymes has used values of 0, 0.4, 1.0 and 2.0 km^{-1} for conditions ranging from zero absorption to foggy or smoky atmospheres. Simpson quotes values from Glasstone (1962) of 0.4, 1.0 and 2.0 km^{-1} for visual ranges of 10, 5 and 2 km, respectively.

A more fundamental treatment has been given by Simpson (1984 SRD R304). This SRD method involves the separate computation of the transmissivities based on absorption and on scattering and each of these transmissivities is calculated for a set of discrete 'windows' spanning the range of wavelengths. The overall atmospheric transmissivity is then obtained as the product of the transmissivities based on absorption and on scattering.

For the transmissivity based on absorption the approach followed is based on the transmission windows method of Elder and Strong (1953) and is as follows. The water absorption bands occur at wavelength $\lambda = 1.1$, 1.38, 1.87, 2.7 and 6.0 μm and the carbon dioxide bands at 2.7, 4.3 and 14.5 μm. The wavelength spectrum from 0.72 to 15.0 μm is divided into 8 windows, as shown in Table 16.56, separated by the water and carbon dioxide bands.

For a given window i the transmissivity based on absorption τ_{ai} is determined from the equations

$$\tau_{ai} = \exp(-A_i w^{\frac{1}{2}}) \qquad w < w_i \qquad [16.13.75a]$$

$$\tau_{ai} = k_i (w_i/w)^{\beta_i} \qquad w > w_i \qquad [16.13.75b]$$

where w is the concentration of water in the atmosphere (pr mm), w_i is the value of w which causes absorption in window i to go from weak band to strong band absorption (pr mm), and A_i, k_i and β_i are constants. The units for water content refer to precipitable water (pr mm). Equation 16.13.75 is based on curve fitting of the plots given by Elder and Strong and on extensions by Simpson. Values of the parameters are given in Table 16.57.

Table 16.56 *Window limits for estimation of atmospheric transmissivity (Simpson, 1984 SRD R304) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Window No.	*Window boundaries,* (λm)
I	0.72–0.94
II	0.94–1.13
III	1.13–1.38
IV	1.38–1.90
V	1.90–2.70
VI	2.70–4.30
VII	4.30–6.0
VIII	6.0–15.0

Table 16.57 *Parameters for estimating the absorption effects on atmospheric transmissivity (Simpson, 1984 SRD R304) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Window No.	A_i	k_i	b_i	w_i
I	0.0305	0.800	0.112	54
II	0.0363	0.765	0.134	54
II	0.1303	0.830	0.093	2.0
IV	0.2110	0.802	0.111	1.1
V	0.3500	0.814	0.1035	0.35
VI	0.3730	0.827	0.095	0.26
VII	0.9310	0.679	0.194	0.18
VIII	0.5980	0.784	0.122	0.165
I-VIII	0.2110	0.855	0.815	0.6

For scattering transmissivity an empirical approach is taken. This transmissivity is given by the relation

$$\tau_{si} = \exp[-\beta(\lambda_i)x] \qquad [16.13.76]$$

where x is the path length and $\beta(\lambda_i)$ is the scattering coefficient for window i.

The scattering coefficient $\beta(\lambda_i)$ is related to the meteorological, or visible, range V. The meteorological range may be defined by the contrast between the sky and a distant black target. Taking a value of 2% contrast gives the relation

$$V = \frac{1.0}{0.02}\frac{1}{\beta n} \qquad [16.13.77]$$

where n is the refractive index of the scattering particles. Following standard practice in evaluating the visual range at $\lambda = 0.55\mu$m

$$\beta = 3.91/V \qquad \lambda = 0.55 \qquad [16.13.78]$$

A widely used expression relating the scattering coefficient β to the wavelength λ is

$$\beta = A\lambda^{-q} \qquad [16.13.79]$$

where A is a constant and q is an index.

Then from Equations 16.13.76–16.13.79

$$\tau_{si} = \exp\left[-\frac{3.91}{V}\left(\frac{\lambda_i}{0.55}\right)^{-q}x\right] \qquad [16.13.80]$$

The value most often proposed for q is 1.3, but on exceptionally clear days it can be as high as 1.6 and for days in which haze reduces the visible range below 6 km a good estimate may be made from the relation

$$q = 0.585\ V^{\frac{1}{3}} \qquad [16.13.81]$$

The total transmissivity τ_{Ti} for window i is the product of the transmissivities based on absorption and on scattering:

$$\tau_{Ti} = \tau_{ai}\tau_{si} \qquad [16.13.82]$$

The radiation transmitted is then determined as follows. From the theoretical black body radiation spectrum a discrete black body radiation spectrum is derived with the radiation in each window i at a constant value. The discrete spectrum of transmitted radiation is then calculated by multiplying the theoretical values by the total transmissivity τ_{Ti} for each window i. The procedure is illustrated in Figure 16.81.

If desired, the overall transmissivity τ may then be determined as the ratio of the total radiation transmitted to the total black body radiation.

Values of the overall atmospheric transmissivity τ have been tabulated by Simpson. He considers black body flame temperatures of 1000, 1150, 1300, 1450 and 1600 K, ambient air temperatures of 0, 15 and 30°C, relative humidities of 10, 30, 70 and 100%, visual ranges of 2, 5, 10 and 20 km, and actual ranges of from 5 m to 10 km. Some of the meteorological data for the UK given by Simpson are shown in Table 16.58. Values of the atmospheric transmissivity τ obtained by Simpson for some typical meteorological conditions are given in Table 16.59.

Simpson gives comparisons of results obtained with the SRD method with those obtained from the methods of Glasstone, Raj *et al.* and TNO. The Glasstone method gives higher values of the atmospheric transmissivity, which Simpson attributes primarily to the fact that the method neglects absorption. The agreement with the Raj method is better, though the latter gives higher values at the longer distances, which Simpson attributes to the fact that the method neglects scattering. There is good agreement with the TNO method for the conditions where comparison can be made, but the SRD method is more comprehensive in that it takes into account the visual range.

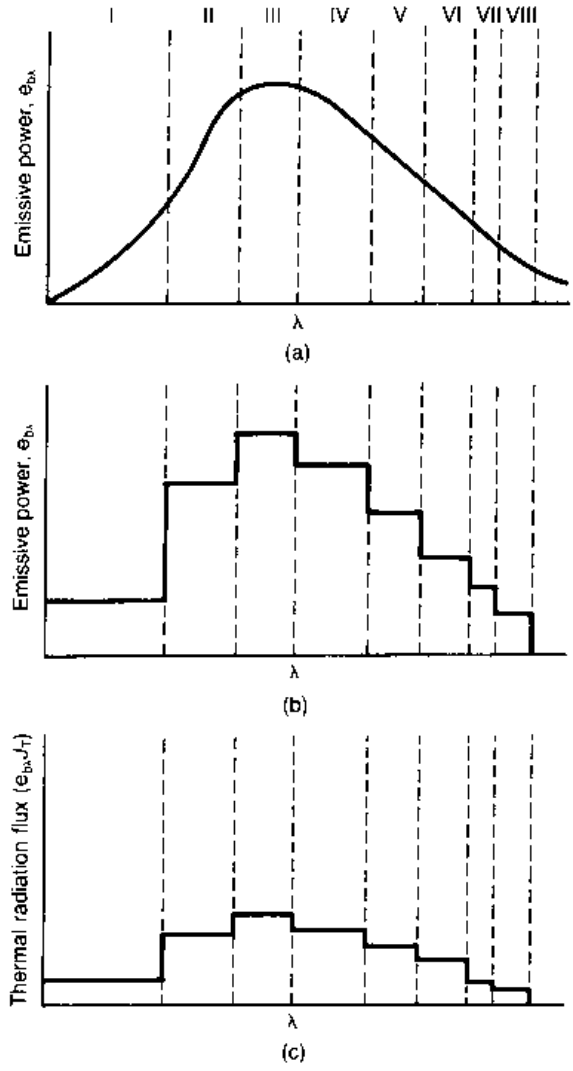


Figure 16.81 *Estimation of radiation transmitted through the atmosphere: (a) theoretical black body radiation spectrum; (b) black body radiation spectrum produced using the procedure outlined; (c) example of the effect of atmospheric transmission on the radiation spectrum (Simpson SRD 1984 R304) J_T, thermal radiation flux (unattenuated) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Table 16.58 *Some meteorological data for the UK relevant to the estimation of atmospheric transmissivity (after Simpson, 1984 SRD R304) (Courtesy of the UKAEA Safety and Reliability Directorate)*

A Maximum air temperatures[a]

Temperature range (°C)	*Relative frequency* (%)
<0	0.7
0.5–5.0	8.8
5.5–10.0	23.5
10.5–15.0	25.6
15.5–20.0	24.0
20.5–25.0	14.0
25.5–30.0	3.2
>30.0	0.2

B Relative humidity (RH) as a function of air temperature[b]

Temperature (°F)	*Relative frequency of RH* (%)						
	40–49	*50–59*	*60–69*	*70–79*	*80–89*	*90–100*	*Total*
54.0–57.9	–	–	–	–	0.6	1.6	2.2
58.0–61.9	–	0.3	1.9	3.5	3.5	5.2	14.4
62.0–65.9	0.4	2.3	6.5	13.0	8.1	5.2	35.5
66.0–69.9	0.6	7.5	8.1	7.1	2.9	0.3	26.5
70.0–73.9	0.3	3.2	4.5	6.1	–	–	14.1
74.0–77.9	–	1.9	2.9	0.3	–	–	5.1
78.0–81.9	–	1.6	0.3	–	–	–	1.9
82.0–85.9	–	0.3	–	–	–	–	0.3
Total	1.3	17.1	24.2	30.0	15.1	12.3	100.0

[a] Kew, 1914–1940.
[b] Calshot, July 1931–1940.

Table 16.59 *Some typical values of atmospheric transmissivity as a function of visual range (Simpson, 1984 SRD R 304) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Visual range (km)	*Range* (m)	
	100	*5000*
1	0.581	0.003
2	0.631	0.046
3	0.656	0.115
4	0.662	0.176
5	0.665	0.224
10	0.665	0.341
50	0.421	
100	0.426	
500	0.426	

A number of other treatments and expressions for atmospheric attenuation have been listed by Bagster and Pitblado (1989) and Satyanarayana, Borah and Rao (1991) as follows:

$$\tau = 1.382 - 0.135 \log_{10}(p_w x) \qquad \text{TNO (1979 } \textit{Yellow Book}\text{)} \qquad [16.13.83]$$

$$\tau = 2.02(p_w x)^{-0.09} \qquad \text{TNO revised} \qquad [16.13.84]$$

$$\tau = 1 - 0.058 \ln x \qquad \text{Major Hazards Assessment Unit} \qquad [16.13.85]$$

where p_w is the partial pressure of water vapour (Pa) and x is the distance (m).

Wayne (1991) has given the following empirical method for the estimation of atmospheric transmissivity. The flame is assumed to be a black or grey body at a temperature of 1500 K, which is chosen as an average value lying between that of a propane fire and that of an LNG fire. His equation is

$$\tau = 1.006 - 0.01171[\log_{10}X(H_2O)] - 0.02368[\log_{10}X(H_2O)]^2 - 0.03188[\log_{10}X(CO_2)] + 0.001164[\log_{10}X(CO_2)]^2 \qquad [16.13.86]$$

with

$$X(CO_2) = L\frac{273}{T} \qquad [16.13.87]$$

$$X(H_2O) = R_H L S_{mm}\left(\frac{288.651}{T}\right) \qquad [16.13.88]$$

where L is the path length (m), R_H is the fractional relative humidity, S_{mm} is the saturated vapour pressure of water at temperature T (mm Hg), T is the atmospheric

temperature (K), $X(CO_2)$ is a function representing the amount of carbon dioxide in the path (m) and $X(H_2O)$ is a corresponding function for water vapour (μm). $X(H_2O)$ is actually defined as the thickness of the uniform liquid layer which would be obtained by notionally condensing the water vapour in an absorbing path of unit cross-sectional area onto its base. $X(H_2O)$ must not exceed a minimum value, assigned as 1 μm, which corresponds to a 10 m path through an atmosphere with $T = 253$ K and $R_H = 0.10$.

Another set of relations is that given by V.C. Marshall (1987), as described in Section 16.15.

16.13.10 Target absorptivity

The fraction of the incident radiant heat which the target absorbs depends on its absorptivity. As already described, absorptivity is closed related to emissivity. An account of the radiation properties of surfaces is given by Sparrow and Cess (1978).

Emissivity is generally tabulated as a property of the material. It should be borne in mind that it is dependent both on the surface condition and on the temperature. The emissivity of many materials has been tabulated by Hottel (McAdams, 1954). Hottel's table includes the following emissivities for steel:

Mild steel (after cleaning)	0.20–0.32
Rolled sheet steel	0.66
Rough steel plate	0.94–0.97

Numerous other tabulations are available.

In most flame radiation applications it is assumed that the absorptivity of a target is equal to the emissivity.

16.13.11 View factor

The treatment of radiant heat transfer from a source to a target is based on the concepts of the enclosure and of the angle factor. Estimation of the radiation incident on a surface requires that account be taken of the radiation arriving on that surface from all directions. In order to do this use is made of the concept of an enclosure for each surface of which the radiation properties and thermal state are defined. An enclosure is not necessarily bounded by solid surfaces; some surfaces may be open.

The other concept is that of the angle factor, also variously known as the shape, geometrical, configuration or view factor. Accounts of angle factors, or view factors, include those given by Hottel (1954), Hamilton and Morgan (1952), McGuire (1953), Sparrow and Cess (1978), Howell (1982) and Siegel and Howell (1991).

An expression for the angle factor between two differential surfaces dA_i and dA_j has been given in Equation 16.13.38 and is

$$dF_{dA_i - dA_j} = \cos\beta_i \cos\beta_j \, dA_j / \pi r^2 \qquad [16.13.89]$$

Similarly

$$dF_{dA_j - dA_i} = \cos\beta_j \cos\beta_i \, dA_i / \pi r^2 \qquad [16.13.90]$$

Hence from Equations 16.13.89 and 16.13.90

$$dA_i \, dF_{dA_i - dA_j} = dA_j \, dF_{dA_j - dA_i} \qquad [16.13.91]$$

Equation 16.13.91 is one of three reciprocity rules. The other two are

$$A_i \, dF_{dA_i - dA_j} = dA_j \, dF_{dA_j - dA_i} \qquad [16.13.92]$$

and

$$A_i \, F_{A_i - A_j} = A_j \, F_{A_j - A_i} \qquad [16.13.93]$$

A further property of angle factors which follows from the principle of energy conservation is

$$\sum_{j=1}^{N} F_{A_i - A_j} = 1 \qquad [16.13.94]$$

where N is the number of surfaces in the enclosure.

There are a number of methods for the derivation of angle factors. They include:

(1) direct integration;
(2) contour integration;
(3) short-cut methods –
  (a) angle factor algebra,
  (b) elongated surfaces,
  (c) string method.

Angle factors have been derived for a large number of standard configurations. There are a number of tabulations available, including those of Hamilton and Morgan (1952), McGuire (1953), Stannard (1977), Sparrow and Cess (1978), Howell (1982) and Siegel and Howell (1991).

It is usual to give for each case the configuration diagram together with the governing equation. Angle factor algebra may be applied to derive an angle factor for a non-standard case from that for a standard case. As an illustration consider the derivation of the angle factor $F_{A_1 - A_4}$ for the system shown in Figure 16.82. Applying the principle of energy conservation

$$A_1 F_{A_1 - A_4} = A_{12} F_{A_{12} - A_4} - A_2 F_{A_2 - A_4} \qquad [16.13.95]$$

where

$$A_{12} = A_1 + A_2 \qquad [16.13.96]$$

Applying the principle further

$$A_{12} F_{A_{12} - A_4} = A_{12} F_{A_{12} - A_{34}} - A_{12} F_{A_{12} - A_3} \qquad [16.13.97]$$

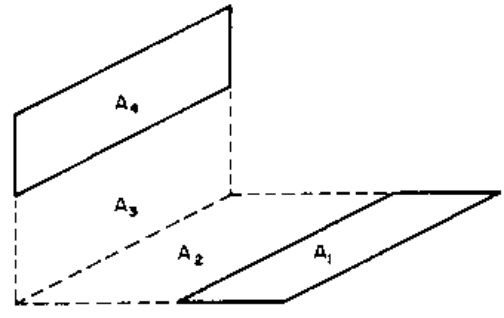


Figure 16.82 *Configuration for illustrative example of angle factor algebra (Sparrow and Cess, 1978) (Courtesy of Brooks/Cole Publishers)*

where

$$A_{34} = A_3 + A_4 \qquad [16.13.98]$$

and hence

$$A_2F_{A_2-A_4} = A_2F_{A_2-A_{34}} - A_2F_{A_2-A_3} \qquad [16.13.99]$$

Substituting from Equations 16.13.97 and 16.13.99 in Equation 16.13.95 yields

$$F_{A_1-A_4} = \frac{1}{A_1}(A_{12}F_{A_{12}-A_{34}} + A_2F_{A_2-A_3} - A_{12}F_{A_{12}-A_3} - A_2F_{A_2-A_{34}}) \qquad [16.13.100]$$

All the angle factors on the right-hand side of Equation 16.13.100 are obtainable from the single standard case of two adjacent surfaces at right angles to each other.

Treatments of view factors specifically oriented to process plant problems include those by Crocker and Napier (1986, 1988a,b) and B.C. Davis and Bagster (1989–).

An common situation is radiation from a source, which can be treated as a point source. In this case the radiation at a spherical surface is

$$E = \frac{Q_r}{4\pi r^2} \qquad [16.13.101]$$

where r is the radius of the spherical surface. Then, for simplicity, neglecting the absorptivity of the target and the atmospheric transmissivity, the heat radiation intensity received by the target is

$$I = \frac{FQ_r}{4\pi l^2} \qquad [16.13.102]$$

where l is the slant distance from the point source to the target.

Then from Equations 16.13.101 and 16.13.102, with Equation 16.13.49 the view factor for this case is

$$F \approx \frac{r^2}{l^2} \qquad [16.13.103a]$$

$$F \approx \frac{r^2}{x^2} \qquad x \approx l \gg r \qquad [16.13.103b]$$

where l is the slant distance and x is the ground distance from the point source to the target.

An important class of flame is elevated flames such as flares and fireballs. These are frequently treated as point sources using Equations 16.13.101–16.13.103.

The view factor is affected by the orientation of the target. The implicit assumption in Equations 16.13.102 and 16.13.103 is that the surface of the target is normal to the line connecting it with the point source. For heat radiation from an elevated point source to a small, or differential, target, a correction is required if the target is, say, vertical or horizontal. For a target which is vertical, so that the line between the point source and the target makes an angle θ with the horizontal, the correction factor to be applied to the view factor is $\cos\theta$. For a target which is horizontal, so that the line between the point source and the target makes an angle ϕ with the vertical, the correction factor is $\cos\phi$. Then, since $\theta + \phi = 90^\circ$, $\cos\phi = \sin\theta$. Hence for these two cases, from Equation 16.13.103

$$F = \frac{r^2}{x^2}\cos\theta \qquad \text{Vertical target} \qquad [16.13.104]$$

$$F = \frac{r^2}{x^2}\sin\theta \qquad \text{Horizontal target} \qquad [16.13.105]$$

Equations for view factors are often expressed not in terms of the angle θ but of the lengths of the two sides of the relevant triangle.

The expressions just given apply to differential elements, or, in practice, small objects. This is generally taken to include the human body. Larger objects, such as storage tanks, are finite surfaces.

Table 16.60 *Some standard view factors that are potentially useful in process radiant heat transfer work*

Configuration	*Reference*[a]
Circular discs	
1. Plane differential element parallel with element:	
1a. Normal to element passes through centre of disc	18
1b. Normal to element does not pass through centre of disc	19
1c. Planes containing element and disc intersect at 90°	20
2. One disc to another parallel disc with centres of both discs along the same axis	23
Right circular cylinders	
3. Plane differential element to cylinder of finite height with normal to element passing through one end of the cylinder and perpendicular to the cylinder axis	26
4. Infinitely long line source to parallel infinitely long cylinder	28
5. Infinitely long plane of finite width to parallel infinitely long cylinder	27
6. Infinitely long cylinder to second infinitely long cylinder of same diameter	30
7. Two concentric cylinders of infinite length	31
8. Two concentric cylinders of finite length	32
Spheres	
9. Spherical point source to sphere	35
10. Plane differential element to sphere	
10a. Normal to element passes through centre of sphere	36
10b. Tangent to element passes through centre of sphere	37
11. Sphere to disc with normal to centre of disc passing through centre of sphere	38
12. Two concentric spheres	41

[a] References are to Siegel and Howell (1991), Appendix C.

For the purposes of determining a view factor, there are a number of different ways of treating a flame. They include treatment as (1) a single point source, (2) multiple point sources, (3) an equivalent radiator or (4) a solid flame. The equivalent radiator (ER) model treats the flame as a two-dimensional surface. For example, the flame on a pool fire is represented as a vertical rectangle. In the solid flame (SF) model the flame is treated as a three-dimensional solid body. For example, the pool fire flame is represented as a vertical cylinder. The point source (PS) and multiple point source (MPS) models are self-explanatory.

Table 16.60 gives references to certain standard view factors listed by Siegel and Howell (1991) which may be of use in work on radiant heat transfer in process plants. Relations for view factors for fireballs, pool fires, flares and jet flames are given in Sections 16.15 and 16.17–16.19, respectively.

16.14 Vapour Cloud Fires

A vapour cloud fire, or flash fire, occurs when a vapour cloud forms from a leak and is ignited, but without creation of significant overpressure. If such overpressure occurs, the event is a vapour cloud explosion (VCE) rather than a vapour cloud fire (VCF).

16.14.1 Vapour cloud fire incidents

Release of flammable vapour from a process plant followed by ignition is a not uncommon occurrence. If the ignition is prompt, the cloud may be modest in size, but if the cloud has time to spread over an appreciable part of the site and is then ignited, a major vapour cloud fire may result. This occurs in only a very small proportion of ignited releases.

Large and destructive vapour cloud fires occurred at Port Newark, New Jersey, in 1951 and at Mexico City, Mexico, in 1984. These and other incidents are described in Section 16.38 and Appendix 4.

16.14.2 Experimental studies

Early experimental work on the combustion of vapour clouds from spills on land has been described by Raj (1977) and work at China Lake in 1978 on spills on water has been described by A.D. Little (1979).

Large-scale tests involving vapour cloud fires from spills of refrigerated liquefied gas on water have been conducted in association with other tests concerned with heavy gas dispersion. The vapour cloud dispersion and fire tests at Maplin Sands have been described by Blackmore, Eyre and Summers (1982) and Hirst and Eyre (1983), and those at China Lake in 1980–81 have been described by Ermak *et al.* (1983). An account of the dispersion tests has already been given in Chapter 15.

The Maplin Sands trials involved the spillage onto the sea, dispersion and, in some cases, combustion of liquefied natural gas (LNG) and refrigerated liquid propane. Both quasi-instantaneous and continuous releases were made. In the trials involving combustion, seven were with LNG and four were with propane. Plate 9 shows the progress of Trial 27 at Maplin.

Ignition was effected by spark igniters located on certain pontoons. In two of the LNG tests flame failure occurred soon after ignition. Moreover, infrared measurements indicated that in several tests, both with LNG and with propane, at least one and sometimes two ignitions were followed by flame failure before the bulk of the cloud ignited. These latter failures were not visible to the eye. Flame failure was attributed to inhomogeneities of the concentration in the cloud.

The instantaneous and continuous releases differed in that, whereas in the latter a pool of liquefied gas was created which gave in effect a pool fire also, in the former there was no pool fire.

The combustion of the vapour cloud involved first burning of the pre-mixed part and then diffusive burning of the fuel-rich part. The flame in the pre-mixed burning did not propagate quickly across the top of the cloud, but remained as a 'wall of fire'.

Expansion of the combustion products was principally in the vertical direction. The unburnt gas was not pushed ahead of the flame front to any significant extent. Where a pool fire occurred, the height of the flame was appreciably greater.

The vapour clouds were made visible by the associated water fog. In the case of the LNG clouds the contour of the lower flammability limit (LFL) lay within that of the fog, and combustion was entirely within the visible fog; some of the visible cloud remained unburned. For the propane clouds the LFL contour lay outside the fog and combustion took place in part outside it.

The flame speeds measured during the combustion were relatively low, and far removed from the figure of 150 m/s often quoted as necessary for the generation of appreciable overpressure. For LNG in Test 27 the flame speed averaged 4 m/s with a maximum of 10 m/s, whilst for propane in Test 51 the corresponding figures were 12 and 20 m/s, respectively.

Pressure deviations measured during the combustion were a maximum of 0.8 mbar for LNG and 0.4 mbar for propane. The maximum deviations were underpressures, the overpressures being rather less. The form of the decay of the overpressure was that the overpressure was inversely proportional to the distance.

With regard to thermal radiation, the surface emissive power of the cloud fires was measured as 173 kW/m^2 for both LNG and propane. For the pool fires the values obtained were 203 kW/m^2 for LNG but 43 kW/m^2 for propane. The authors suggest that a value of 200 kW/m^2 may be representative for larger vapour cloud fires and for LNG pool fires. The lower value for propane pool fires is in accordance with results for pool fires of propane on land, as described below.

The account of the combustion tests in the Coyote trials described by Ermak *et al.* (1983) gives broad confirmation of these findings. The tests involved 40 m^3 spills of LNG onto water. Again the flame velocities were modest. They lay in the range 11.9–18.9 m/s for wind speeds of 4.6–10.0 m/s, the values of the flame speed less the wind speed being 6.4–12.9 m/s. The flame velocities appeared to be high near the ignition source, whether a flare or a jet, and fell off rapidly. There was no indication of significant flame acceleration. The flame heights were somewhat higher than in the Maplin tests.

16.14.3 Empirical features

The foregoing description indicates some of the empirical features of a vapour cloud fire. A further account is given by Crawley (1982). The conditions favouring a vapour

cloud fire are a prolonged release in conditions of poor dispersion.

Two main types of flame behaviour have been assumed. Raj and Emmons (1975) conceive the burning as a 'wall of fire', whilst Fay and Lewis (1977) propose the formation of a fireball by the rising thermal. No fireball effect is mentioned in connection with the tests just described. The wall of fire mode occurs in the combustion of the fuel-rich portion. Overall, the combustion is usually not especially rapid or violent, the flame progressing through the cloud at a speed of several metres per second.

Strictly, a vapour cloud combustion which generates overpressure has to be classed as a vapour cloud explosion. In practice, the latter term tends to be reserved for cases where the explosion causes significant destruction. For vapour cloud fires, the overpressures vary from the imperceptible up to those which may cause some window damage.

A vapour cloud fire may cover a wide area, perhaps some thousands of square metres. It results in scorching and depletion of oxygen, with potential for injury and damage. It may initiate BLEVEs and other releases of flammable material which then feed the fire. It also deposits soot.

16.14.4 Modelling of vapour cloud fires

The hazard from a vapour cloud fire is usually assessed by considering dispersion of the vapour cloud and ignition of this cloud and making some relatively simple assumption concerning the effects inside and outside the cloud.

In many assessments no explicit model of a vapour cloud fire has been utilized. Instead it has been assumed that: the contours of the burning cloud are those of the lower flammability limit concentration; persons inside the cloud suffer a defined degree of injury, generally a fatal injury; and those outside the cloud are subject to a level of thermal radiation based on an assumed surface emissive power at the edge of the burning cloud.

16.14.5 Eisenberg, Lynch and Breeding model

An early model for a flash fire is the vulnerability model by Eisenberg, Lynch and Breeding (1975). The vapour cloud is assumed to be a half ellipsoid with volume V_r and area A_r given by the equations

$$V_r = \frac{2\pi}{3}\sigma_x\sigma_y\sigma_z(r_l^3 - r_u^3) \qquad [16.14.1]$$

$$A_r = \frac{2\pi}{3}(\sigma_x^2 + \sigma_y^2 + \sigma_z^2)(r_l^2 + r_u^2) \qquad [16.14.2]$$

with

$$r_l = 2\ln\left[\frac{2m}{(2\pi)^{\frac{3}{2}}\sigma_x\sigma_y\sigma_z k_l}\right]^{\frac{1}{2}} \qquad [16.14.3]$$

$$r_u = 2\ln\left[\frac{2m}{(2\pi)^{\frac{3}{2}}\sigma_x\sigma_y\sigma_z k_u}\right]^{\frac{1}{2}} \qquad [16.14.4]$$

where A_r is the area of radiation of the hot gas layer (m^2), k_l is the concentration at the lower explosive limit (kg/m^3), k_u is the concentration at the upper explosive limit (kg/m^3), m is the total mass of vapour released (kg), r_l is a parameter of the cloud at the lower explosive limit, r_u is a parameter of the cloud at the upper explosive limit, V_r is the volume of the hot gas layer (m^3), and σ_x, σ_y and σ_z are dispersion coefficients in the downwind, crosswind and vertical (x, y and z) directions, respectively (m).

The heat loss q from the gas is predominantly by radiation, so that

$$q \approx A_r\sigma(\epsilon_g T_g^4 - \epsilon_a T_a^4) \qquad [16.14.5]$$

where q is the heat loss by radiation (W), T_a is the absolute temperature of the environment (K), T_g is the absolute temperature of the hot gas (K), ϵ_a is the emissivity of the environment, ϵ_g is the emissivity of the hot gas and σ is the Stefan–Boltzmann constant ($= 5.67 \times 10^{-8} W/m^2K^4$).

The layer of radiating gas may be expected to be some tens or even hundreds of meters thick. Under these conditions the gas emissivity does not change much with layer thickness or temperature and has a value of about 0.5. The authors replace Equation 16.14.5 by the approximate relation

$$q \approx A_r\sigma(T_g^4 - T_a^4) \qquad [16.14.6]$$

The gas emissivity of unity in Equation 16.14.6 includes an allowance for the other modes of heat transfer.

The heat loss is also given by

$$q = -c_p\rho V_r\frac{dT_g}{dt} \qquad [16.14.7]$$

where c_p is the specific heat of the hot gas layer (J/kg K), t is the time (s) and ρ is the density of the hot gas layer (kg/m^3). The hot gas layer is nearly always mostly air.

Equating the heat flows in Equations 16.14.6 and 16.14.7 gives

$$\frac{dT_g}{dt} = -k(T_g^4 - T_a^4) \qquad [16.14.8]$$

with

$$k = \frac{A_r\sigma}{c_p\rho V_r} \qquad [16.14.9]$$

Equation 16.14.8 has the solution

$$t = \frac{1}{2kT_a^3}\left\{\left[\tan^{-1}\left(\frac{T_g}{T_a}\right) - \frac{1}{2}\ln\left(\frac{T_g - T_a}{T_g + T_a}\right)\right] - \left[\tan^{-1}\left(\frac{T_{gi}}{T_a}\right) - \frac{1}{2}\ln\left(\frac{T_{gi} - T_a}{T_{gi} + T_a}\right)\right]\right\} \qquad [16.14.10]$$

where subscript i denotes the initial value.

Equation 16.14.10 may be rewritten in terms of the half-life $t_{\frac{1}{2}}$ of the fire, or the time at which

$$T_g = \frac{T_{gi} + T_a}{2} \qquad [16.14.11]$$

Then

$$t_{\frac{1}{2}} = \frac{1}{2kT_a^3}\left[\tan^{-1}\left(\frac{\beta+1}{2}\right) - \tan^{-1}\beta - \frac{1}{2}\ln\left(\frac{\beta+1}{\beta+3}\right)\right] \qquad [16.14.12a]$$

or, in the equivalent form given by the authors,

$$t_{\frac{1}{2}} = \frac{1}{2kT_a^3}\left[\tan^{-1}(1/\beta) - \tan^{-1}\left(\frac{2}{\beta+1}\right) - \frac{1}{2}\ln\left(\frac{\beta+1}{\beta+3}\right)\right] \quad [16.14.12b]$$

with

$$\beta = T_{gi}/T_a \quad [16.14.13]$$

where $t_{\frac{1}{2}}$ is the half-life of the flash fire (s).

The effective thermal radiation intensity is given by

$$I_r = \sigma(T_g^4 - T_a^4) \quad [16.14.14]$$

where I_r is the effective thermal radiation intensity of the flash fire (W/m^2).

The effective time duration t_{eff} is

$$t_{eff} = 3t_{\frac{1}{2}} \quad [16.14.15]$$

where t_{eff} is the effective time duration of the flash fire (s). The initial value of the absolute temperature of the hot gas T_{gi} is taken as the adiabatic flame temperature.

16.14.6 Raj and Emmons model

Another flash fire model is that of Raj and Emmons (1975). This model takes into account the speed of the flame propagating through the cloud. The assumptions made are that during the combustion of a vapour cloud there is a turbulent flame front propagating into the unburned cloud at a constant velocity which is roughly proportional to the wind speed, and that at high gas concentrations there is a tall flame plume at the edge of the unburned cloud.

This model is represented in Figure 16.83 in which a flame front is propagating at constant velocity S into an unburned cloud of depth D with a flame base of width W and a flame height H above the top of the cloud.

The treatment of flame height is based on the pool fire model of F.R. Steward (1964). The observed height of such flames is approximately twice that of the base ($H/W = 2$). Application of the conservation equations gives a relation between the flame height and the upward velocity of the gases. Then from a mass balance on the triangle formed by the flame and the base, a relation may be derived between the flame height H and the flame speed S.

This treatment forms the basis of the semi-empirical equation given by Raj and Emmons for the flame height of a flash fire:

$$H = 20D\left[\frac{S^2}{gD}\left(\frac{\rho_o}{\rho_a}\right)^2 \frac{wr^2}{(1-w)^3}\right]^{\frac{1}{3}} \quad [16.14.16]$$

with

$$S = 2.3U_w \quad [16.14.17]$$

where D is the cloud depth (m), g is the acceleration due to gravity (m/s^2), H is the visible flame height (m), r is the stoichiometric air–fuel mass ratio, S is the flame speed, or 'burning speed' (m/s), U_w is the wind speed (m/s), w is a parameter, ρ_a is the density of air (kg/m^3) and ρ_o is the density of the fuel–air mixture (kg/m^3).

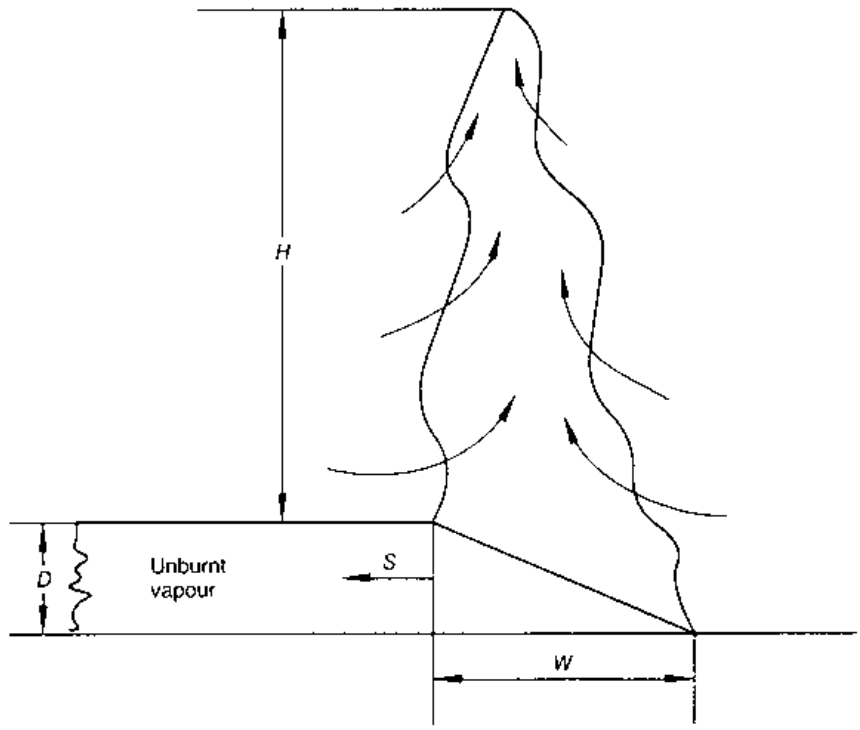


Figure 16.83 *Flame at the edge of a burning vapour cloud (after Raj and Emmons, 1975; CCPS, 1994/15) (Reproduced by permission of the American Institute of Chemical Engineers)*

The parameter w represents the inverse of the volumetric expansion due to combustion in the plume and is strongly dependent on the composition of the cloud. For a cloud of pure vapour, $w \approx 1/9$, assuming the vapour is hydrocarbon, whilst for a cloud of stoichiometric composition or leaner, $w = 0$.

The application of the relation for w given by Raj and Emmons is somewhat complex. As described below, the Center for Chemical Process Safety (CCPS) has developed an alternative and more straightforward equation.

The expression for the flame speed S is derived by Raj and Emmons from a limited number of experimental observations.

The heat flux incident on a receptor may be estimated from Equation 16.13.49.

16.14.7 CCPS model

The set of hazard models given in the CCPS *Fire and Explosion Model Guidelines* (1994/15) includes a model for flash fires. The model is essentially that of Raj and Emmons with a modification of the expression for the parameter w. For this the CCPS gives

$$w = 0 \qquad \phi \leq \phi_{st} \qquad [16.14.18a]$$

$$w = \frac{\phi - \phi_{st}}{\alpha(1 - \phi_{st})} \qquad \phi > \phi_{st} \qquad [16.14.18b]$$

where α is the constant pressure expansion ratio for stoichiometric combustion, ϕ is the volumetric concentration of fuel (v/v) and the subscript st denotes stoichiometric. For hydrocarbons the value of α is typically about 8.

In applying the model for the estimation of thermal radiation the CCPS propose the use of the following two assumptions: (1) during the propagation of the flash fire, the cloud is stationary and is fixed and homogeneous in composition; and (2) the time-dependent flame surface is a plane cross-section moving through the cloud at the flame speed.

16.14.8 Considine and Grint model

Considine and Grint (1985) have given a model for a flash fire in the form of graphs of the distance to particular levels of fatal injury. This model is described in Section 16.39.

16.15 Fireballs

Another significant fire hazard is that from fireballs. Accounts of fireballs include those by Gayle and Bransford (1965), R.W. High (1968), Hardee and Lee (1973), Strehlow and Baker (1976), Fay and Lewis (1977), V.C. Marshall (1977a, 1987), Hardee, Lee and Benedick (1978), Hasegawa and Sato (1977, 1978), Fay, Desgroseillers and Lewis (1979), Williamson and Mann (1981), A.F. Roberts (1981/82, 1982), Crawley (1982), Lihou and Maund (1982), Moorhouse and Pritchard (1982), W.E. Baker *et al.* (1983), Pietersen (1985), Jaggers *et al.* (1986), Roper *et al.* (1986), D.M. Johnson and Pritchard (1991) and the CCPS (1994/15).

Most treatments of fireballs relate to liquefied gas. Here a distinction needs to be made between a fireball resulting from the bursting of a pressure vessel and one resulting from the formation of a vapour cloud. In the first case the bursting may occur under fire conditions and be part of a BLEVE or it may occur in the absence of fire. Momentum forces predominate if a fireball is formed from the bursting of a vessel, and buoyancy forces predominate in one formed from a vapour cloud.

There are two other types of event which may give rise to a 'fireball'. One is the ignition of a release on a liquefied gas pipeline, where the jet flame is preceded by a fireball in which unignited gas is burned. The other is an eruption in hot oil giving rise to a release of burning vapour. This is exemplified by the event that occurs when water is added to burning fat in a chip pan. Eruptions of burning vapour have occurred in some storage tank fires.

An instance has also occurred of a congested fireball following rupture and release of the flammable contents of a reactor into a building.

The type of fireball of particular interest, however, is that which occurs as part of a BLEVE and it is this type which is mainly treated here.

A quite different type of fireball is that associated with the explosion of a propellant or high explosive. Such fireballs are discussed in the next section.

Some studies on fireballs are given in Table 16.61.

16.15.1 Fireball incidents

Incidents involving fireballs are not uncommon. They usually occur as part of a BLEVE when a vessel ruptures after it has been engulfed in fire or has been subjected to a directed flame. The vessels principally liable to such conditions are storage vessels, rail tank cars and road tankers.

Fireball incidents are generally associated with BLEVE incidents. BLEVEs are considered in Chapter 17, which contains in Table 17.37 a list of incidents involving fireballs with and without BLEVE.

A massive BLEVE fireball occurred at Crescent City, Illinois, in 1970 with an estimated diameter of 150–200 m (Case History A50). Other major BLEVE fireball incidents include those at Houston, Texas, in 1971 (Case History A53), Lynchburg, Virginia, in 1972 (Case History A59), Kingman, Arizona, in 1973 (Case History A63), Oneonta, New York, and West St Paul, Minnesota, in 1974, and Belt, Montana, in 1976. The estimated diameters of the fireballs at Houston, Kingman and Belt were 300 m. The disaster at Mexico City in 1985, described in Appendix 4, involved a series of fireballs from BLEVEs. Other fireball incidents have occurred at Eagle Pass, Texas, in 1975, Goldona, Virginia, in 1977, and Donnellson, Iowa (Case History A91) and Lewisville, Arkansas, in 1978. The estimated diameter of the fireball at Donnellson was 610 m and of those at Goldonna and Lewisville 320 and 310 m, respectively. The fireball at Crescent City is shown in Plate 33.

16.15.2 Experimental studies

Experimental research on fireballs has taken three main forms treating fireballs generated by (1) explosives and propellants, (2) gas-filled bubbles and balloons and (3) containers undergoing BLEVE.

Early experimental investigations of fireballs were concerned with fireballs from propellants. Gayle and Bransford (1965) obtained data from 47 tests and incidents with the mass of combined propellant (fuel + oxidizer) in the range 10–250 000 lb.

Table 16.61 *Some studies of fireballs*

Experimental study on fireballs of propellants	Gayle and Bransford (1965)
Theoretical study of fireballs of rocket propellants	R.W. High (1968)
Theoretical study of fireballs of propellants	Bader, Donaldson and Hardee (1971)
Theoretical study of fireballs from bursting vessels	Hardee and Lee (1973, 1975)
Experimental and theoretical study of fireballs from a stationary vapour cloud	Fay and Lewis (1977); Fay, Desgroseilliers and Lewis (1979)
Theoretical study of LNG fireballs	Hardee, Lee and Benedick (1978)
Experimental and theoretical study of fireballs following liquid flash-off	Hasegawa and Sato (1977, 1978)
Experimental and theoretical study of fireballs from bursting vessels	Maurer *et al.* (1977); Giesbrecht *et al.* (1980)
Review of experimental and theoretical work on fireballs and of case histories and assessment of hazard	V.C. Marshall (1977a, 1987)
Experimental study on fireballs	A. Baker (1979)
Review of experimental and theoretical work on fireballs and correlation of principal features of fireball behaviour	A.F. Roberts (1981/82, 1982)
Experimental and theoretical study of fireballs	Lihou and Maund (1982)
Review of experimental and theoretical work on fireballs	Moorhouse and Pritchard (1982)
Theoretical study of fireballs	Jaggers *et al.* (1986); Roper *et al.* (1986)
Experimental study of BLEVEs, including fireballs	D.M. Johnson and Pritchard (1991)

A correlation for the diameter of the fireball of the propellant of the Saturn rocket of NASA, based on tests, has been given by R.W. High (1968).

Taking first small scale tests, Fay and Lewis (1977) studied the fireball from hydrocarbon fuels held initially inside soap bubbles with volumes in the range 20–190 cm^3. Hasegawa and Sato (1977) carried out a series of 22 tests on fireballs of *n*-pentane held in glass spheres with a fuel mass in the range 3.1–6.2 kg. These authors also performed a further series of 32 tests on fireballs with a fuel mass in the range 3.1—31.0 kg. Hardee, Lee and Benedick (1978) have described tests on fireballs of pure and pre-mixed methane held in balloons and polyethylene bags, with quantities in the range 0.1–10 kg. A.F. Roberts (1981/82) reports two unpublished tests by A. Baker (1979) with a fuel mass of the order of 10 kg. Lihou and Maund (1982) have described experiments on fireballs from hydrocarbons in bubbles with a fuel mass in the range 0.07–6 g.

Of the larger scale tests, most have been associated with BLEVEs. C. Anderson *et al.* (1975) have described a test on a fully loaded 125 m^3 rail tank car which was made to suffer a BLEVE. A single fireball experiment with a fuel mass of 452 kg has been described by Maurer *et al.* (1977) and Giesbrecht *et al.* (1980). In the work at Bundesanstalt für Materialprüfung (BAM) on fire engulfed vessels, described by Schulz-Forberg, Droste and Charlett (1984), Droste and Schoen (1988) and Schoen, Probst and Droste (1989), several of the vessels were taken to the point of a BLEVE. Other larger scale experiments on BLEVEs have been reported by D.M. Johnson and Pritchard (1991). In this work the mass of fuel involved was of the order of 1–2 te.

16.15.3 Empirical features

A fireball from the bursting of a pressure vessel containing liquefied gas is observed to pass through a number of fairly well defined phases.

The development of a full-scale fireball is captured in the National Fire Protection Association (NFPA) film on BLEVEs. Crawley (1982) has described the development based on a frame-by-frame analysis of this film. The fireball passes through three phases: (1) growth, (2) steady burning and (3) burnout. The growth phase may be divided into two intervals, each of about 1 second duration. In the first interval the flame boundary is bright with yellowish-white flames indicating a flame temperature of about 1300°C. The fireball grows to about half its final diameter. Calculation indicates that fuel droplets of less than 4–5 mm diameter would vaporize. This would give good mixing with air at the droplet scale. There would also be good bulk mixing.

In the second interval of the growth phase, the fireball grows to its final volume, but about 10% of the surface is dark and sooty with the rest being white, yellowish-orange or light red, indicating flame temperatures in the range 900–1300°C, with an estimated effective flame temperature of 1100–1200°C.

In the second phase, which lasts some 10 seconds, the fireball, which is now roughly spherical, is no longer growing. At the start of this phase it begins to lift off. It rises and changes to the familiar mushroom shape. The estimated effective flame temperature is 1100–1200°C.

In the third phase, which lasts some 5 seconds, the fireball remains the same size, but the flame become less sooty and more translucent.

Figure 16.84 illustrates the typical development of a fireball as a function of time.

The experimental work has also yielded useful information on aspects such as the fraction of the fuel which participates in the fireball, the fireball diameter and duration, the fraction of heat of combustion which is radiated, and the surface emissive power of the fireball. These aspects are discussed below.

16.15.4 Modelling of fireballs

The modelling of fireballs covers the following aspects: (1) the fireball regime, (2) the mass of fuel in the fireball, (3) the fireball development and time scales, (4)

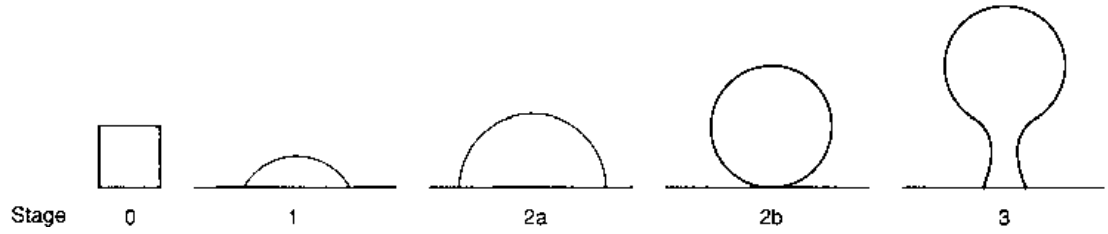


Figure 16.84 *Development of a typical fireball from a source at ground level*

the fireball diameter and duration, (5) the heat radiated and (6) the view factor.

The treatment of the heat radiated from a fireball is a good illustration of the different approaches which may be taken to the modelling of fires in process plants. Specifically, there are three different ways of determining the heat radiated. One is to assume that it is a given fraction of the heat released. Another is to assume a given value for the heat radiated from the flame surface, or surface emissive power. The third is to estimate the heat radiated from the flame properties, such as flame temperature and emissivity.

Models of fireballs are of two broad types: correlations of diameter and duration time, and fundamental models.

In order to maintain some consistency with the notation of the original authors, the symbols M and W are both used for mass.

16.15.5 Fireball regimes

As stated earlier, there are two basic scenarios for the fireball of a liquefied gas. The case of prime interest is a fireball resulting from the bursting of a pressure vessel. The other case is a fireball from the burning of a stationary vapour cloud at atmospheric pressure.

These two situations constitute quite different regimes. The duration times for these are: for the bursting vessel where momentum forces dominate

$$t_d \propto M^{\frac{1}{3}} \qquad [16.15.1]$$

and for a vapour cloud where buoyancy forces dominate

$$t_d \propto M^{\frac{1}{6}} \qquad [16.15.2]$$

where M is the mass of fuel (kg) and t_d is the duration time (s).

For the situation where initially there is high momentum, a change of regime occurs as the momentum declines and gravity slumping begins.

The case of prime interest here is the bursting of a vessel, but that of a stationary vapour cloud is also treated in Sections 16.15.17 and 16.15.18.

16.15.6 Mass of fuel

The mass of fuel in the fireball depends on the fraction of fuel which flashes off and on the further fraction which forms liquid spray.

For propane the relation between the theoretical adiabatic flash fraction and the liquid temperature and vapour pressure is shown in Figure 16.85 (A.F. Roberts, 1981/82). The 35% flash fraction occurs at 21°C and the 50% flash faction at 45°C.

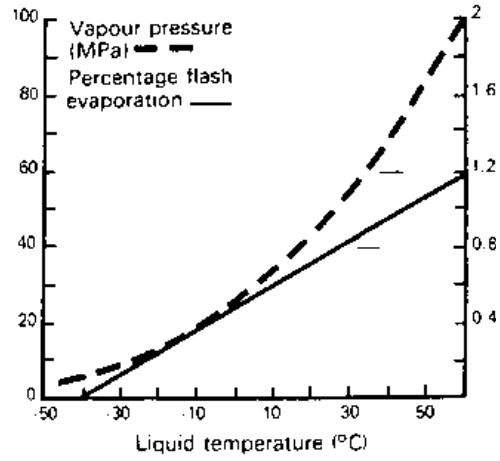


Figure 16.85 *Relation between the theoretical adiabatic flash fraction and temperature and vapour pressure prior to rupture for a fireball (A.F. Roberts, 1981/82). (Reproduced by permission of the* Fire Safety Journal)

Hasegawa and Sato (1977) found that when the theoretical adiabatic flash fraction reaches 35% virtually all the liquid released burns as a fireball.

From this, A.F. Roberts (1982) derives the relations

$$f = \frac{M}{M_r} = 0 \qquad \phi = 0 \qquad [16.15.3a]$$

$$f = 1 \qquad \phi \geq 0.35 \qquad [16.15.3b]$$

where f is the fraction of fuel released entering the fireball, M is the mass of fuel in the fireball (kg), M_r is the mass of liquid released (kg) and ϕ is the fraction of liquid vaporized. Hence by linear interpolation

$$f = \frac{\phi}{0.35} \qquad 0 < \phi < 0.35 \qquad [16.15.3c]$$

This treatment is broadly equivalent to the rule of thumb commonly used for fireballs that the fraction of the fuel released which participates in the fireball is three times the flash fraction. This is the method used by the CCPS (1994/15) to determine the mass of fuel in the fireball.

Both the equations and the rule of thumb just quoted evidently derive from the Hasegawa and Sato's work. An essentially similar approach is taken in the treatment given by V.C. Marshall (1987), as described in Section 16.15.20, except that he makes a distinction between

summer and winter conditions. Another commonly used, and conservative, approach is to assume that all the fuel released enters the fireball.

16.15.7 Fireball development and time scales

A fireball is of relatively short duration, but it passes in its life cycle through several distinct stages which need to be carefully defined if confusion is to be avoided. A discussion of these stages and of the associated time scales is given by A.F. Roberts (1981/82).

He distinguishes three distinct stages of fireball development. Stage 1 involves the rapid mixing of the fuel with air and rapid combustion of the fuel and is dominated by the initial momentum of release. In Stage 2, the residual fuel is mixed with air already in the cloud or entrained into it and is burned; this stage is more affected by buoyancy and combustion effects and less by the initial momentum. In Stage 3, with combustion essentially complete the fireball rises due to buoyancy, entraining further air and cooling; in this stage the size may be increasing or decreasing depending on the relative rates of air entrainment and of heat loss. These stages of development are illustrated for a small fireball in Figure 16.86.

Roberts defines five time scales. The time t_a is the duration of combustion in a system dominated by initial momentum effects. The time t_b is the duration of combustion in a system dominated by buoyancy effects, and t_c is the duration of combustion in a system dominated by deflagration effects; these are alternatives to time t_a. The time t_d is that at which visible radiation from the fireball ceases. The time t_e is that at which fireball lift-off occurs. Of the three combustion times, that of prime concern here is t_a which is that applicable to a fireball following bursting of a vessel.

16.15.8 Fireball diameter and duration

Fundamental models of fireballs are given below. The most widely used models, however, are essentially correlations of fireball diameter and duration time, of which there are a considerable number.

Various workers have correlated fireball diameter using a relation of the form

$$D = k_1 M^{n_1} \qquad [16.15.4]$$

where D is the diameter of the fireball (m), k_1 is a constant and n_1 is an index.

An early correlation of fireball diameter is that of R.W. High (1968), who gives

$$D = 9.82\, W^{0.320} \qquad [16.15.5a]$$

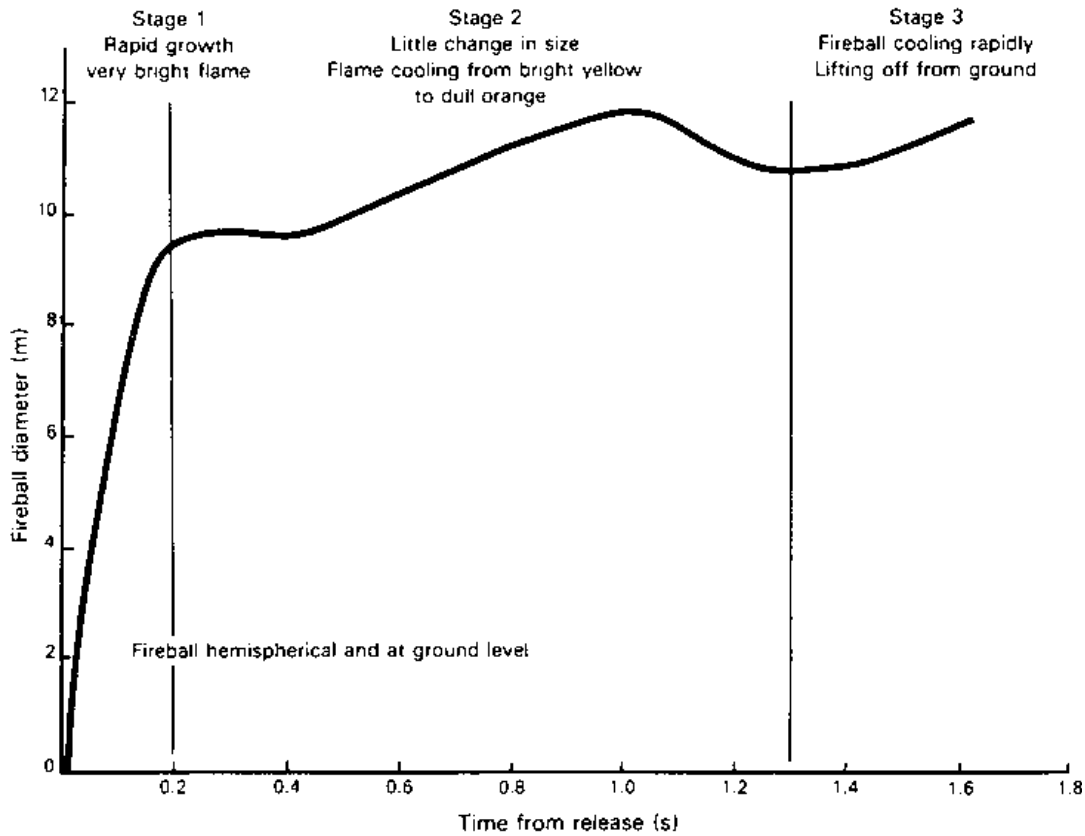


Figure 16.86 *Time scales for the development of a small fireball (A.F. Roberts, 1981/82). (Reproduced by permission of the* Fire Safety Journal)

where D is the diameter of the fireball (ft) and W is the mass of propellant (fuel + oxidizer) (lb). Roberts converts this equation to

$$D = 2.95\ W^{0.320} \qquad [16.15.5b]$$

where D is the fireball diameter (m) and W is the mass of propellant (kg).

Hasegawa and Sato (1978) give for their definitive correlation following their second series of tests

$$D = 5.25\ M^{0.314} \qquad [16.15.6]$$

The available experimental data on, and correlations for, fireball diameters have been reviewed by A.F. Roberts (1981/82) who obtained for hydrocarbons the following relation:

$$D = 5.8\ M^{\frac{1}{3}} \qquad [16.15.7]$$

This is now probably the mostly widely used correlation for fireball diameter.

Most correlations of the duration time t_d are of the form

$$t_d = k_2 M^{n_2} \qquad [16.15.8]$$

where k_2 is a constant and n_2 is an index.

An early equation for duration time is that of R.W. High (1968) who gives the following equation for the persistence time

$$d = 0.232\ W^{0.320} \qquad [16.15.9a]$$

where d is the persistence time (s) and W is the mass of propellant (lb). Roberts converts this to the equivalent relation

$$t_d = 0.49\ M^{0.320} \qquad [16.15.9b]$$

Hasegawa and Sato give equations for the duration time of their first set of experiments with smaller fireballs ($M < 6.1$ kg) and for the combined sets of experiments with smaller and larger fireballs. The exponents in their equations are 0.097 and 0.181, respectively.

These two sets of correlations reflect, therefore, the difference in the exponent discussed in Section 16.15.5.

Here it is the fireball from the bursting of a vessel which is of prime interest. From a review of the experimental data and correlations for duration time, Roberts obtains

$$t_d = 0.45\ M^{\frac{1}{3}} \qquad [16.15.10]$$

Equation 16.15.10 is not applicable, however, to larger masses, where the regime is dominated by buoyancy rather than momentum. These different regimes have been described in Section 16.15.5 and are treated again in the model of Jaggers, Roper *et al.* in Section 16.15.18. In the buoyancy-dominated regime, the index of M is approximately $\frac{1}{6}$ rather than $\frac{1}{3}$ as in the momentum-dominated regime. The Major Hazards Assessment Panel (MHAP) (1988 LPB 82) has therefore proposed the following modification:

$$t_d = 0.45\ M^{\frac{1}{3}} \qquad M < 30\,000 \qquad [16.15.11]$$

$$t_d = 2.6\ M^{\frac{1}{6}} \qquad M > 30\,000 \qquad [16.15.12]$$

Pietersen (1985) gives for LPG fireballs the correlations

$$D = 6.48\ M^{0.333} \qquad [16.15.13]$$

$$t_d = 0.852\ M^{0.26} \qquad [16.15.14]$$

A summary of correlations of fireball diameter and duration time is given in Table 16.62. Further comparisons of such correlations are given by Bagster and Pitblado (1989), Satyanarayana, Borah and Rao (1991) and the CCPS (1994/15).

16.15.9 Heat radiated

There are three methods of estimating the heat radiated by a fireball. These are based on (1) the heat evolved and radiated, (2) the surface emissive power and (3) the flame temperature and emissivity.

The heat evolved may be obtained from the heat of combustion of the fuel.

For the fraction of heat radiated Roberts states that the work of Hasegawa and Sato suggests a value of the

Table 16.62 *Some correlations of fireball diameter and duration time for hydrocarbons*[a]

Diameter D (m)	*Duration time,* t_d (s)	*Material*	*Reference*
$5.55\ M^{0.333}$	–	Propane	Hardee and Lee (1973)
$6.36\ M^{0.325}$	$2.57\ M^{0.167}$	Hydrocarbons	Fay and Lewis (1977); Hardee, Lee and Benedick (1978)
$5.25\ M^{0.314}$	$1.07\ M^{0.181}$	*n*-Pentane	Hasegawa and Sato[b] (1978)
$5.8\ M^{0.333}$	$0.45\ M^{0.333}$	Hydrocarbons	A.F. Roberts (1981/82, 1982)
$5.88\ M^{0.333}$	$1.09\ M^{0.167}$	Propane	Williamson and Mann (1981)
$5.72\ M^{0.333}$	$0.45\ M^{0.333}$	Butane	Lihou and Maund (1982)
$5.33\ M^{0.327}$	$0.923\ M^{0.303}$	Hydrocarbons	Moorhouse and Pritchard (1982)
$6.48\ M^{0.325}$	$0.852\ M^{0.26}$	LPG	Pietersen (1985)
$5.5\ M^{0.333}$	$0.38\ M^{0.333}$	Hydrocarbons	V.C. Marshall (1987)

[a] Sources: Lihou and Maund (1982); Bagster and Pitblado (1989); Satyanarayana, Borah and Rao (1991); and original papers.
[b] These authors' earlier correlation (1977) was $D = 5.28\ M^{0.277}$.

order of 0.25. He also proposes the following relation based on the results of these workers:

$$F_r = 0.27\,P^{0.32} \qquad 1.35 \leq P \qquad [16.15.15]$$

where F_r is the fraction of heat radiated and P is the vapour pressure at the moment of release (MPa). He states that extrapolation up to $P = 6$ MPa, about the highest pressure of interest, gives $F_r = 0.48$. A more refined treatment by Roberts is described below.

Another rule of thumb for the fraction of heat radiated is that given by Hymes (1983, SRD R275) which is that the fraction of heated radiated for a vessel bursting below the set pressure of the pressure relief valve may be taken as 0.3 and that for one bursting above this pressure as 0.4. A commonly used value for the fraction of heat radiated from a fireball is 0.3.

Several workers have quoted values of the surface emissive power. Estimates made by Roberts of the heat flux at the surface of the fireballs in the work of Hasegawa and Sato are in the range 141–196 kW/m^2 with individual values up to 450 kW/m^2. A review of the surface emissive power of fireballs by Moorhouse and Pritchard (1982) concludes that the realistic range is 150–300 kW/m^2. In large scale experiments on BLEVEs, D.M. Johnson and Pritchard (1991) obtained surface emissive powers in the range 250–350 kW/m^2. Considine, Grint and Holden (1982) use a value of 350 kW/m^2 for hazard assessment. These figures are appreciably higher than those for pool fires.

Based on the work of Roberts, the MHAP give the following relation for surface emissive power:

$$E = 235\,P^{0.39} \qquad P \leq 2 \qquad [16.15.16]$$

where E is the surface emissive power (kW/m^2) and P is the pressure (MPa). The limit on pressure given is equivalent to a limit on the surface emissive power of 308 kW/m^2. A surface emissive power commonly used for fireballs is 350 kW/m^2.

The fraction of heat radiated is used in conjunction with the point source model of a fireball and the surface emissive power is used in conjunction with the solid flame model. The two quantities are not independent but are linked via the surface area of the fireball. Given a fireball diameter, and hence a surface area, a particular value of the surface emissive power implies a corresponding value of the fraction of heat radiated.

With regard to fireball temperature, Roberts states that the values which he derives for the surface emissive power in the work of Hasegawa and Sato, just mentioned, are in the range consistent with flame temperatures of 1000–1400°C, a flame emissivity of unity, and 50–100% excess air. As described in Section 16.15.3, Crawley (1982) has used film of an actual fireball to obtain estimates of effective flame temperature of the order of 1100–1200°C.

The proportionalities between the diameter D, the duration time t_d and the mass of fuel M given in Section 16.15.8 have an important consequence. The heat generation is proportional to the mass M of the fireball, the heat loss per unit time is proportional to the surface area A, the heat loss at a given fraction of the duration time is proportional to the product At_d, the surface area A is proportional to $M^{\frac{2}{3}}$ and the duration time t_d is proportional to $M^{\frac{1}{3}}$. It follows, according to this model, that for a given fuel the heat radiation and temperature at a given fraction of the duration time are the same for all masses of fuel, or, in other words, that there is a single heat radiation and temperature profile.

16.15.10 Fireball scenarios

Before considering the view factor it is necessary to say something about the scenarios usually considered in the modelling of thermal radiation from a fireball. The approach commonly taken is to assume that the fireball is a sphere with its base just touching the ground and that its diameter and duration are given by one of the sets of correlations just described.

A target close to the fireball may be engulfed by it and it is of interest to know the furthest distance at which engulfment occurs. For this purpose there are two fireball geometries which may be used. One is that of a fireball which is essentially spherical but slightly settled on the ground. This corresponds to the shape of the fireball over most of its life and the engulfment distance approximates to the radius of the fireball. The other geometry is that of a hemispherical fireball. This corresponds to the shape of the fireball during its initial expansion and the engulfment distance then approximates to the radius of this hemispherical fireball, being greater than the spherical case by a factor of about 1.25 ($2^{\frac{1}{3}}$). The period of engulfment in the hemispherical fireball is much shorter.

In the near field estimates of the thermal radiation from a fireball are subject to some inaccuracy.

The set of view factors available for fireballs covers both the near and far fields and includes view factors for targets beneath an elevated fireball. The more complex expressions for the view factor are those applicable to such near field situations.

16.15.11 View factor

For a spherical fireball the thermal radiation intensity at the surface is

$$E = \frac{Q_r}{4\pi r^2} \qquad [16.15.17]$$

where E is the surface emissive power, Q_r is the heat radiated and r is the radius of the fireball.

The heat received I by a target normal to the surface of the fireball is

$$I = \alpha\tau FE \qquad [16.15.18]$$

$$= \frac{\alpha\tau FQ_r}{4\pi r^2} \qquad [16.15.19]$$

$$= \frac{\alpha\tau Q_r}{4\pi l^2} \qquad [16.15.20]$$

where l is the distance between the centre of the fireball and the target, α is the absorptivity of the target and τ is the atmospheric transmissivity. Hence from Equations 16.15.19 and 16.15.20 the view factor F for such a target is

$$F = \frac{r^2}{l^2} \qquad [16.15.21]$$

A set of view factors for fireballs covering other situations has been given by the CCPS (1994/15). For

a horizontal surface at a ground distance x the view factor is

$$F = \frac{r^2 h}{(x^2 + h^2)^{\frac{3}{2}}} \qquad [16.15.22]$$

where h is the height of the centre of the fireball ($h \geq r$) and x is the distance from the point directly beneath the centre of the fireball and the target, or the ground distance.

The corresponding expression for a vertical surface is limited to the case where the surface is not directly beneath the fireball:

$$F = \frac{r^2 x}{(x^2 + h^2)^{\frac{3}{2}}} \qquad x > r \qquad [16.15.23]$$

In the far field ($x \approx l \gg h$) Equation 16.15.23 reduces to Equation 16.15.21.

For the case where the surface is beneath the fireball expressions exist both for a vertical surface and for a surface of any inclination. The latter is given here as being the more general case. Here two situations have to be considered, as shown in Figure 16.87. In Figure 16.87(a) the target 'sees' the whole fireball, whilst in Figure 16.87(b) it does not, the part of the fireball marked X being out of sight. The expressions for the view factor in these two separate cases are

$$F = \frac{r^2}{l^2} \cos\theta \qquad \theta \leq \frac{\pi}{2} - \phi \qquad [16.15.24]$$

$$F = \frac{1}{2} - \frac{1}{\pi} \sin^{-1}\left[\frac{(l^2 - r^2)^{\frac{1}{2}}}{l \sin\theta}\right] + \frac{r^2}{\pi l^2} \cos\theta \cos^{-1}\left[-\frac{(l^2 - r^2)^{\frac{1}{2}}}{r} \cos\theta\right] - \frac{1}{\pi l^2}(l^2 - r^2)^{\frac{1}{2}}(r^2 - l^2 \cos^2\theta)^{\frac{1}{2}} \qquad \theta > \frac{\pi}{2} - \phi \qquad [16.15.25]$$

The case to which these latter equations apply is a rather special one and, as indicated above, near field estimates are subject to some inaccuracy.

Crocker and Napier (1988a) have given relations for the view factor for a spherical fireball just touching the ground for the three cases of (1) a large vertical target, (2) a differential vertical target and (3) a differential horizontal target. Their expressions are equivalent, respectively, to Equation 16.15.21, or Equation 16.13.103; Equation 16.13.104; and Equation 16.13.105. These authors also treat the case of an elevated fireball.

16.15.12 Point source model

One of the simplest practical models for a fireball is the point source model. For this model the heat received by the target is

$$I = \frac{\alpha \tau F_r Q}{4\pi l^2} \qquad [16.15.26]$$

where Q is the heat release rate (kW).

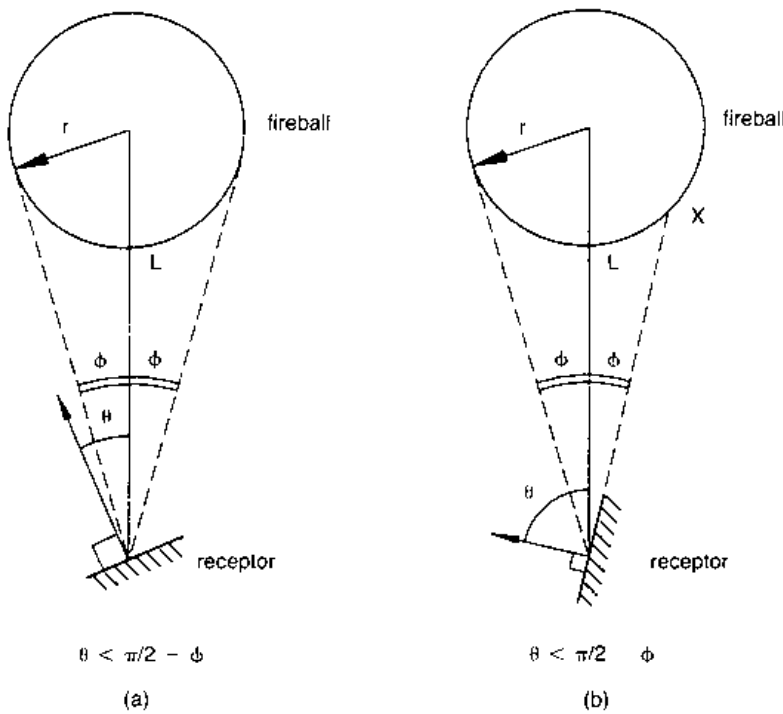


Figure 16.87 *View factor for fireballs (after CCPS, 1994/15): (a) the target 'sees' the whole fireball; and (b) the target 'sees' only part of the fireball (Courtesy of the American Institute of Chemical Engineers)*

Hymes (1983 SRD R275) has given a version of this model which effectively incorporates a combustion rate and an allowance for the effect on this of the mass of fuel. Introducing the term α to put the model on the same basis as the previous equation gives

$$I = \frac{2.2\alpha\tau F_r \Delta H_c M^{0.67}}{4\pi l^2} \quad [16.15.27]$$

where ΔH_c is the heat of combustion (kJ/kg).

16.15.13 Solid flame model

The other main alternative for practical use is the solid flame model

$$I = \alpha\tau FE \quad [16.15.28]$$

16.15.14 Fireball modelling

Fireball models in the form of correlations of diameter and duration time have already been described. There are also a number of more fundamental models. Such models include those by Bader, Donaldson and Hardee (1971), Hardee and Lee (1973), Fay and Lewis (1977), Hardee, Lee and Benedick (1978), A.F. Roberts (1981/82, 1982), Williamson and Mann (1981), Lihou and Maund (1982), Jaggers *et al.* (1986), Roper *et al.* (1986) and V.C. Marshall (1987). Some of these models are now described.

16.15.15 Bader, Donaldson and Hardee model

An early fundamental model of a fireball is that by Bader, Donaldson and Hardee (1971). The model is for the fireball of a propellant such as the Saturn fireball. The fireball is assumed to be a homogeneous, isothermal body which is spherical throughout. Other assumptions are that the rate of addition of propellant is constant, that no air enters the fireball either during or after the reaction period, that all the propellant participates in the reaction, and that the fireball radiates as a black body. For simplicity, it is assumed that the burnout and lift-off times coincide.

For a high temperature fireball such that the difference $\Delta\rho$ between the density of the air ρ_a and the density of the fireball gas ρ is approximated by $\Delta\rho \approx \rho$, the buoyancy force is

$$F_B = \tfrac{4}{3}\pi r^3 \rho g \quad [16.15.29]$$

and the fluid resistance force of the fireball gas is

$$F_R = \frac{2}{3}\pi r^3 \rho \left[\frac{2}{r}\left(\frac{dr}{dt}\right)^2 - \frac{d^2r}{dt^2}\right] \quad [16.15.30]$$

where F_B is the buoyancy force (N/m^2), F_R is the resistance force (N/m^2), g is the acceleration due to gravity (m/s^2), r is the radius of the fireball (m), ρ is the density of the fireball (kg/m^3) and t is time (s). Equating these two equations yields

$$\frac{d^2r}{dt^2} - \frac{2}{r}\left(\frac{dr}{dt}\right)^2 + 2g = 0 \quad [16.15.31]$$

In this equation the first term is the inertia term and the second the added mass term due to the displacement of air by the gaseous products. The solution of Equation 16.15.31 is

$$r = \frac{g}{3}t^2 \quad [16.15.32]$$

The radius of the fireball at burnout, and on lift-off, is

$$r_b = \left(\frac{3}{4\pi\rho}\right)^{\frac{1}{3}} W_b^{\frac{1}{3}} \quad [16.15.33]$$

where r_b is the radius of the fireball at burnout (ft), W_b is the mass of propellant, and therefore of the fireball, at burnout (lb) and ρ is the density of the fireball gas (lb/ft^3). Taking a value of $\rho = 0.0055\,lb/ft^3$ yields

$$r_b = 3.51\, W_b^{\frac{1}{3}} \quad [16.15.34]$$

Combining Equations 16.15.32 and 16.15.33 gives for the burnout time

$$t_b = 0.572\, W_b^{\frac{1}{3}} \quad [16.15.35a]$$

$$\approx 0.6 W_b^{\frac{1}{3}} \quad [16.15.35b]$$

where t_b is the burnout time (s).

For the growth of the fireball

$$R = W/t \quad [16.15.36]$$

$$= W_b/t_b \quad [16.15.37]$$

where R is the rate of addition of propellant (lb/s), W is the mass of the fireball (lb), t is time (s) and the subscript b denotes burnout.

From Equations 16.15.35b and 16.15.37

$$R = \tfrac{5}{3}\, W_b^{\frac{5}{6}} \quad [16.15.38]$$

The radius of the fireball may then be written as

$$r = \left(\frac{3Rt}{4\pi\rho}\right)^{\frac{1}{3}} \quad [16.15.39]$$

where r is the radius of the fireball and ρ is its density. Utilizing Equation 16.15.38

$$r = \left(\frac{5W_b^{\frac{5}{6}}}{4\pi\rho}\right)^{\frac{1}{2}} t^{\frac{1}{3}} \quad [16.15.40]$$

16.15.16 Hardee and Lee model

Another early fireball model is that by Hardee and Lee (1973). This model applies to the fireball following the rupture of a vessel containing a liquefied flammable gas. The assumptions made reflect those of the model of Bader, Donaldson and Hardee, with the changes necessary to treat the case in hand. It is assumed that a vapour cloud grows into which the rate of addition of fuel is assumed to be constant. Ignition occurs when the mixture is stoichiometric. The fireball is homogeneous, isothermal and spherical. Other assumptions are that all the available fuel is burned, that the fireball radiates as a black body, and that the burnout and lift-off times coincide. The model given is similar to that of Bader, Donaldson and Hardee and includes Equations 16.15.33, 16.15.35b, 16.15.38 and 16.15.40.

The authors obtain for a propane fireball a relation equivalent in SI units to

$$D = 5.55\, M^{\frac{1}{3}} \quad [16.15.41]$$

where D is the diameter of the fireball (m) and M is the mass of fuel (kg).

This model has been further developed by Hardee, Lee and Benedick (1978), who apply it to a fireball of LNG. Equation 16.15.35b may be rewritten in SI units as

$$t_b = 0.684\ W_b^{\frac{1}{6}} \quad [16.15.42]$$

and then as

$$t_b = 0.684(W_b/W_f)^{\frac{1}{6}} W_f^{\frac{1}{6}} \quad [16.15.43]$$

where t_b is the burnout time (s), W_b is the mass of the fireball, including air, at burnout (kg), W_f is the mass of fuel (kg). For a stoichiometric mixture of methane and air $W_b/W_f = 18.3$. Substituting this value in Equation 16.15.43 yields

$$t_b = 1.11\ W_f^{\frac{1}{6}} \quad [16.15.44]$$

Further, taking the density ρ as $0.160\,kg/m^3$ and the value of W_b/W_f as 18.3, and utilizing Equation 16.15.44 in Equation 16.15.40 yields

$$r = 3.12\ W_f^{\frac{1}{3}} \quad [16.15.45]$$

where r is the radius of the fireball (m).

The resulting correlations for fireball diameter and duration time are therefore

$$D = 6.24\ M^{0.333} \quad [16.15.46]$$

$$t_b = 1.11\ M^{0.167} \quad [16.15.47]$$

A critique of this model of an LNG fireball has been given by Gillette (1980), who makes detailed criticisms of the model itself and suggests that for LNG the occurrence of 'fireballs' is a speculation.

16.15.17 Fay and Lewis model

The model by Fay and Lewis (1977) is applicable to the quite different situation of a fireball formed from a compact, stationary cloud of pure fuel vapour ignited at the edge. In this scenario, the combustion products move upwards, promoting mixing with the air. When the volume of these products becomes comparable with the initial volume of the vapour, the mixture of fuel, air and products begins to rise, burning more vigorously as it accelerates, consuming virtually all the fuel.

In modelling the combustion, it is assumed that the volume of the unburned vapour is negligible compared with that of the products. Thus, for example, the volume of the products of the stoichiometric, adiabatic combustion of methane is 83 times that of the fuel vapour.

The authors state that it can be shown by dimensional analysis that the following proportionalities hold:

$$r_p \propto gt^2 \quad [16.15.48]$$

$$r_p \propto V_f^{\frac{1}{3}} \quad [16.15.49]$$

$$z_p \propto V_f^{\frac{1}{3}} \quad [16.15.50]$$

$$t_p \propto V_f^{\frac{1}{6}}/g^{\frac{1}{2}} \quad [16.15.51]$$

where r is the radius of the cloud, t is the time, V_f is the volume of the initial cloud of fuel, z is the height of the centre of the cloud and subscript p denotes the products.

The growth of the cloud is modelled drawing on the entrainment hypothesis of B.R. Morton, Taylor and Turner (1956). The volumetric rate of growth is taken as being proportional to the product of the local surface area and the local rise velocity:

$$\frac{d}{dt}\left(\frac{4}{3}\pi r^3\right) = \beta 4\pi r^2 \frac{dz}{dt} \quad [16.15.52]$$

where β is the entrainment coefficient. The order of magnitude of β is one.

Integrating Equation 16.15.52 with the boundary conditions $r = 0$; $z = 0$ yields

$$r = \beta z \quad [16.15.53]$$

Hence

$$z = \frac{1}{\beta}\left(\frac{3V}{4\pi}\right)^{\frac{1}{3}} \quad [16.15.54]$$

Equating the forces of buoyancy and of the rate of change of vertical momentum

$$\frac{d}{dt}\left[\frac{4}{3}\pi r^3 \rho_p \left(\frac{dz}{dt}\right)\right] = \frac{4}{3}\pi r^3 g(\rho_a - \rho_p) \quad [16.15.55]$$

where ρ_a is the density of air.

Utilizing Equation 16.15.52 in the integration of Equation 16.15.55 gives

$$r = \frac{g\beta}{14}\left(\frac{\rho_a - \rho_p}{\rho_p}\right)t^2 \quad [16.15.56]$$

Hence

$$t = \left[\frac{14\rho_p}{g\beta(\rho_a - \rho_p)}\right]^{\frac{1}{2}}\left(\frac{3V}{4\pi}\right)^{\frac{1}{6}} \quad [16.15.57]$$

where V is the volume of the fireball.

The radius r, height z and duration t have their maximum values when the cloud volume V equals the volume V_p of the combustion products. For a hydrocarbon C_nH_m

$$V_p = \left[\frac{m\phi + 4.762(4n + m)}{4\phi}\right]\left(\frac{T_p}{t_r}\right)V_f \quad [16.15.58]$$

where T_p is the absolute temperature of the products, T_r is that of the reactants, V_f is the volume of the fuel, V_p is that of the products and ϕ is the equivalence ratio.

The authors treat β and ϕ as parameters to be determined. From soap bubble experiments they obtain for the entrainment coefficient an average value of $\beta = 0.285$. This is in reasonable agreement with the values given by Morton, Taylor and Turner. For the equivalence ratio the average value is $\phi = 0.217$, which corresponds to about 4.5 times the stoichiometric amount of air.

16.15.18 Jaggers, Roper *et al.* model

Studies of the conditions under which the buoyancy and momentum regimes apply have been described by Jaggers, Roper and co-workers (Jaggers *et al.*, 1986; Roper *et al.*, 1986).

Jaggers *et al.* (1986) give a set of relations based on dimensional analysis. For the case where the release

velocity is low and buoyancy forces dominate those of momentum, they obtain

$$t_b \propto \frac{1}{g^{\frac{1}{2}}}\left(\frac{M}{\rho_a}\right)^{\frac{1}{6}} \quad [16.15.59]$$

whilst for the other limiting case where the release velocity is high and momentum forces dominate those of buoyancy

$$t_b g^{\frac{1}{2}}\left(\frac{\rho_a}{M}\right)^{\frac{1}{6}} \propto \frac{g^{\frac{1}{2}}}{v_o}\left(\frac{\rho_a}{M}\right)^{-\frac{1}{6}} \quad [16.15.60]$$

Hence

$$t_b \propto \frac{1}{v_o}\left(\frac{M}{\rho_a}\right)^{\frac{1}{3}} \quad [16.15.61]$$

where M is the mass of fuel, t_b is the burning time, v_o is the mean release velocity and ρ_a is the density of air. The mean release velocity v_o is defined as the ratio of the initial momentum of the release to the mass of fuel released.

16.15.19 Roberts model

The fireball model which is most widely used is probably that of A.F. Roberts (1981/82, 1982). The model comprises both fundamental and correlation models and covers the whole range of features of practical interest.

Fireball development

Roberts takes as his starting point for fireball growth the model by Hardee and Lee (1973). From this he obtains for a hemispherical fireball

$$r = \left(\frac{4\alpha M t}{\pi \rho_a}\right)^{\frac{1}{4}} \quad [16.15.62]$$

$$\frac{dr}{dt} = \left(\frac{\alpha M}{64\pi\rho_a}\right)^{\frac{1}{4}} t^{-\frac{3}{4}} \quad [16.15.63]$$

$$V = \frac{2\pi}{3}\left(\frac{4\alpha M t}{\pi\rho_a}\right)^{\frac{3}{4}} \quad [16.15.64]$$

where M is the mass of fuel released (kg), r is the cloud radius (m), t is the time (s), V is the cloud volume (m^3), α is the momentum per unit mass (m/s) and ρ_a is the density of air (kg/m^3).

The concentration of the fuel may be determined from the mass released M and from the volume V of the cloud.

The term α is a function of the vapour pressure of the liquid in the vessel prior to failure. For a vapour pressure less than the atmospheric pressure, $\alpha = 0$. For propane at 28°C and a vapour pressure of 1 MPa, $\alpha = 220$ m/s.

For propane, the cloud volume given by Equation 16.15.64 may be written as

$$V = 118(Mt)^{\frac{3}{4}} \quad [16.15.65]$$

Since for propane at the lower flammability limit the volume of the cloud is approximately $30M$, the time t' required for the cloud to fall below the lower flammability limit (s) is

$$t' = \frac{35}{\alpha}M^{\frac{1}{3}} \quad [16.15.66]$$

Some typical values for this time are

M (kg)	α (m/s)	t' (s)
1000	220	1.6
100 000	220	7.4

The time t_g required for the transition from a regime dominated by momentum effects to one dominated by gravitational slumping is derived by Roberts from the work of Jagger and Kaiser (1981). The criterion given for transition is

$$N = \frac{gr\Delta\rho}{\rho_a(dr/dt)^2} = 1 \quad [16.15.67]$$

where $\Delta\rho$ ($= \rho_v - \rho_a$) is the density difference between the vapour and the air (kg/m^3).

For the Hardee and Lee model

$$N = g\frac{(\rho_v - \rho_a)}{\rho_v}\frac{6t}{\alpha} \quad [16.15.68]$$

Then for $N = 1$

$$t_g = \frac{\rho_v}{6g(\rho_v - \rho_a)}\alpha \quad [16.15.69]$$

where t_g is the time to the transition from control by momentum to control by gravity slumping (s).

For propane from Equation 16.15.68 and with $N = 1$

$$t_g = 0.05\alpha \quad [16.15.70]$$

Fireball volume and diameter

For the fireball volume and diameter Roberts gives the following treatment. The volume V of the fireball at the mean temperature T_f is

$$V = \frac{M_a + M_f}{\rho_f} \quad [16.15.71]$$

$$= \frac{(M_a + M_f)T_f}{\rho_o T_o} \quad [16.15.72]$$

and the enthalpy H is

$$H = c(M_a + M_f)(T_f - T_o) \quad [16.15.73]$$

where c is the specific heat (kJ/kg K), H is the enthalpy rise of the fireball (kJ), M_a is the mass of air in the fireball (kg), M_f is the mass of fuel in the fireball (kg), T_f is the absolute mean temperature of the fireball (K), T_o is the absolute initial temperature of the reactants (K), ρ_f is the density of the products at temperature T_f (kg/m^3) and ρ_o is the density of the products at temperature T_o (kg/m^3).

Then from Equations 16.15.72 and 16.15.73

$$V = \frac{M_a + M_f}{\rho_o}\left[1 + \frac{H}{T_o c(M_a + M_f)}\right] \quad [16.15.74]$$

and hence

$$D = \left\{\frac{6}{\pi}\left[1 + \frac{H}{T_o c(M_a + M_f)}\right]\frac{M_a/M_f + 1}{\rho_o}\right\}^{\frac{1}{3}} M_f^{\frac{1}{3}} \quad [16.15.75]$$

where D is the diameter of the fireball (m).

Different relations are required for the enthalpy H, depending on whether the mixture is fuel or oxygen

rich. If R is the value of the ratio M_a/M_f for the stoichiometric mixture, then

$$H = \frac{\eta M_a Q}{R} \qquad \frac{M_a}{M_f} < R \text{ (fuel rich)} \qquad [16.15.76a]$$

$$H = \eta M_f Q \qquad \frac{M_a}{M_f} > R \text{ (oxygen rich)} \qquad [16.15.76b]$$

where Q is the heat of combustion (kJ/kg) and η the thermal efficiency. The thermal efficiency η takes account of heat losses during growth to the maximum diameter and losses due to unburned fuel.

Roberts uses Equation 16.15.75 to explore the effect of the air/fuel ratio parameter M_a/RM_f and the thermal efficiency η on the constant k_1 in Equation 16.15.4 for fireball diameter. The value of this constant is 5.8 for $M_a/RM_f = 1$ and $\eta = 1$ and it is relatively insensitive to M_a/RM_f over the range 0.8–3.0 and to η over the range 0.75–1.0.

Duration time

Roberts argues that the behaviour of larger fireballs ($M > 5$ kg) appears to differ from that of smaller ones, and obtains for larger fireballs only the relation

$$t_d = 0.83\, M^{0.316} \qquad [16.15.77]$$

where t_d is the duration time (s).

The experimental correlations for duration time t_d therefore lie between equation (16.15.10) and the relation

$$t_d = 0.90\, M^{\frac{1}{3}} \qquad [16.15.78]$$

The data of Baker also lie between the lines given by Equations 16.15.10 and 16.15.78. The relation recommended by Roberts for the duration time t_d is Equation 16.15.10.

For the lift-off time t_e Roberts quotes the equation given by Hardee and Lee

$$t_e = 1.1\, M^{\frac{1}{6}} \qquad [16.15.79]$$

where t_e is the lift-off time (s). Lift-off is determined by buoyancy effects and the exponent of $\frac{1}{6}$ is well established for such effects.

The exponent of $\frac{1}{6}$ in Equation 16.15.79 for lift-off time t_e compares with that of $\frac{1}{3}$ in Equation 16.15.10 for the duration time t_d. Thus the lift-off time t_e may be less or greater than the duration time t_d. Roberts quotes the following typical figures obtained from these equations:

M (kg)	t_d (s)	t_e (s)
200	2.6	2.6
50 000	16	6.7

Thus for smaller fireballs combustion will tend to be complete before lift-off occurs, while for larger ones lift-off will tend to occur while combustion is still taking place. It is the duration time t_d which is used to characterize the period during which the fireball radiates heat.

Heat radiated

In the model given by Roberts for heat radiation from the fireball, it is assumed that such radiation occurs as a square wave pulse of duration t_d. The basic equation for heat radiation is

$$Q_r = \frac{F_r M \Delta H_c}{t_d} \qquad [16.15.80]$$

where ΔH_c is the heat of combustion (kJ/kg), F_r is the fraction of heat radiated and Q_r is the heat radiation rate (kW).

The intensity of thermal radiation at a target, neglecting target absorptivity and atmospheric transmissivity effects, is then

$$I = \frac{Q_r}{4\pi l^2} \qquad [16.15.81]$$

where I is the radiation intensity received by a target perpendicular to the direction of radiation (kW/m^2) and l is the distance from the centre of the fireball to the target (m). The relation between the term $(1/4\pi l^2)$ in Equation 16.15.81 and the view factor is given in Section 16.15.11.

Roberts' treatment of the fraction F_r of heat radiated has already been described, but for completeness is restated here. He quotes values in the range 0.2–0.4 as typical of both pool fires and fireballs. He also analyses the data of Hasegawa and Sato (1978), shown in Figure 16.88, and derives from these a relation between the heat radiation factor and the vapour pressure prior to rupture

$$F_r = 0.27\, P^{0.32} \qquad [16.15.82]$$

where F_r is the fraction of heat radiated and P is the vapour pressure just prior to rupture (MPa).

Equation 16.15.82 is thus derived for data with vapour pressures up to 1.35 MPa, but Roberts suggests it may be extrapolated up to 6 MPa at which pressure the value of F_r is 0.48.

Summary

Roberts' model for a fireball from a bursting vessel may be summarized as follows. The mass of fuel in the fireball is given by Equation 16.15.3, the diameter of the fireball by Equation 16.15.7, the duration time of the fireball by Equation 16.15.10, the fraction of heat radiated by Equation 16.15.82, the total heat radiated by Equation 16.15.80, and the thermal radiation received by the target (neglecting the target absorptivity and atmospheric transmissivity effects) by Equation 16.15.81.

16.15.20 Marshall model

Another model which is readily applied to practical situations is that by V.C. Marshall (1987). This model is based essentially on correlations for diameter and duration time, but again deals with the other features of practical interest.

The model may be summarized as follows. For the mass of fuel in the fireball

$$M = 2\phi\, M_s \qquad \text{Winter} \qquad [16.15.83a]$$

$$M = 3\phi\, M_s \qquad \text{Summer} \qquad [16.15.83b]$$

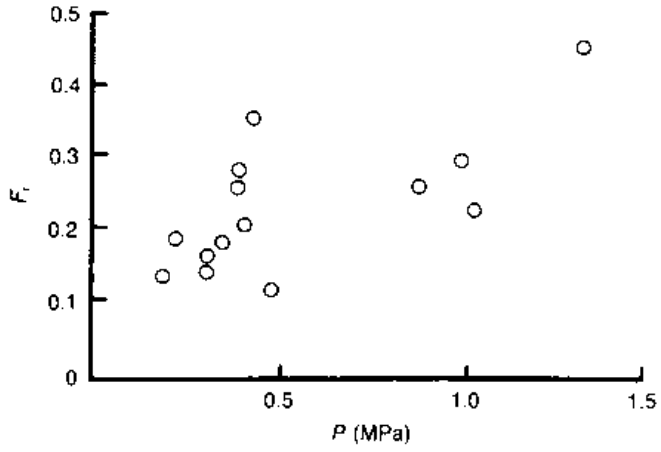


Figure 16.88 *Relation between the fraction of heat radiated and the vapour pressure prior to rupture for a fireball (A.F. Roberts, 1981/82). Data from Hasegawa and Sato (1978); 6.2 kg of pentane in each test (Reproduced by permissionof the* Fire Safety Journal)

where M is the mass of fuel entering the fireball (te), M_s is the mass of fuel in the vessel (te) and ϕ is the theoretical adiabatic flash fraction (TAFF).

The radius and duration time of the fireball are

$$R_{FB} = 27.5\, M^{\frac{1}{3}} \qquad [16.15.84]$$

$$D_{FB} = 3.8\, M^{\frac{1}{3}} \qquad [16.15.85]$$

where D_{FB} is the duration time of the fireball (s) and R_{FB} is its radius (m).

The heat released and fraction of heat radiated are

$$E_T = HM \qquad [16.15.86]$$

where E_T is the heat released (J) and H is the heat of combustion (J/te). The fraction F_R of heat radiated is taken as 0.3.

The radiative power and radiative power density are then

$$P_{FB} = E_T F_R / D_{FB} \qquad [16.15.87]$$

$$P_D = P_{FB} / V_{FB} \qquad [16.15.88]$$

where P_D is the radiative power density (W/m^3), P_{FB} is the radiative power (W) and V_{FB} is the volume of the fireball (m^3).

The thermal radiation intensity is

$$I_T = \frac{P_{FB}}{4\pi R_T^2} \qquad [16.15.89]$$

where I_T is the unattenuated thermal radiation at the radius where the target is located (W/m^2) and R_T is the distance from the centre of the fireball to the target (m).

The effective surface temperature is

$$T_e = \left[\frac{E_T F_R}{\sigma D_{FB}(4\pi R_{FB}^2)}\right]^{\frac{1}{4}} \qquad [16.15.90]$$

where T_e is the effective fireball temperature (K) and σ is the Stefan–Boltzmann constant.

The atmospheric attenuation is given by

$$\tau = X - 0.12 \log_{10} R_T \qquad [16.15.91]$$

where τ is the atmospheric transmissivity and X is a parameter. The values of X are 1.0, 0.96 and 0.92 for relative humidities of 0.2, 0.5 and 1.0, respectively.

The thermal radiation received by the target is then

$$I_{TA} = \tau I_T \qquad [16.15.92]$$

where I_{TA} is the thermal radiation received by the target, taking account of attenuation by the atmosphere (W/m^2).

Taking for hydrocarbons a heat of combustion of 47 MJ/kg yields

$$E_T = 47 \times 10^9 M \qquad [16.15.93]$$

$$P_{FB} = 1.24 \times 10^{10}\, F_r\, M^{\frac{2}{3}} \qquad [16.15.94]$$

$$I_T = 2.94 \times 10^8\, M^{\frac{2}{3}} / R_T^2 \qquad [16.15.95]$$

As an illustration, consider the example given by Marshall of the fireball from a release of 20 te of propane. Then

$M = 20$ te

$H = 47 \times 10^9$ J/te

$R_{FB} = 74.6$ m

$D_{FB} = 10.3$ s

$E_T = 9.4 \times 10^{11}$ J

$F_R = 0.3$

$P_{FB} = 2.73 \times 10^{10}$ W

$I_T = 2.17 \times 10^9 / R_T^2$

16.15.21 CCPS method

A model for a fireball was given in the CCPS *QRA Guidelines* (1989/5). A summary of this model has been published by Prugh (1994). A more recent model is that included in the CCPS *Fire and Explosion Model*

Guidelines (1994/15), where it is included as part of the treatment of BLEVEs.

The method covers the following features: (1) the mass of fuel participating in the fireball, (2) the diameter and duration of the fireball, (3) point source and solid flame models of the fireball, (4) the surface emissive power of the fireball, (5) the view factor and (6) the atmospheric transmissivity.

The mass of fuel in the fireball is taken as three times the flash fraction or, if this figure exceeds unity, the mass released. For the fireball diameter and duration, use is made of Roberts' equations (Equations 16.15.7 and 16.15.11 or 16.15.12).

Both point source and solid flame models are used. For the point source method use is made of Hymes' Equation 16.15.27. For the solid flame method Equation 16.15.28 is used in conjunction with a surface emissive power of 350 kW/m^2.

The view factors are those attributed to the CCPS in Section 16.15.11, especially Equation 16.15.23.

The atmospheric transmissivity is taken in the sample problem as unity, although several relationships are given for it.

The *Guidelines* give a sample problem involving BLEVE of a tank truck containing propane, for which two treatments are presented, one using the point source model and the other using the solid flame model.

16.15.22 Congested fireballs

A type of fireball which somewhat resembles one arising from a BLEVE is that which can occur following sudden rupture of a vessel, such as a reactor, with release of flammable contents and immediate ignition. An instance of this is given by Cates (1992), who terms the incident which he describes a 'congested fireball'. Since such an event gives an appreciable overpressure, it is considered in Chapter 17.

16.15.23 Fireballs on pipelines

An account of a fireball and a subsequent jet flame resulting from the rupture of a pipeline containing liquefied propane has been given by Hirst (1984, 1986). The development of the fireball is shown in Plate 14. The photographs show at −10 s an unignited cylindrical cloud, at 1 s partial ignition, at 3 s a mushroom cloud and at 8 s an elongated jet flame. This work is described in more detail in Section 16.19.

16.16 Fireballs from Explosives

The models just given are for fireballs of hydrocarbons. There may also be a requirement for a model of the fireball from a condensed phase explosive. There is a limited amount of information available on the fireballs from solid and liquid propellants and from high explosives. Accounts of work in this area are given by Jarrett (1952), Gayle and Bransford (1965), Rakaczky (1975), Stull (1977), Mallory (1980), Kovar *et al.* (1982), W.E. Baker *et al.* (1983) and Gilbert, Lees and Scilly (1994d).

16.16.1 Fireball incidents

Not surprisingly, data on the features of fireballs in incidents involving the explosion of high explosives are sparse. An exception is the explosion which occurred in Peterborough in the UK in 1989 on a truck carrying commercial explosives. According to the report by the HSE (1990c) the load was essentially nitroglycerine-based explosives with a total mass of some 800 kg. From the fact that one fireman was engulfed in flames at a distance of 18 m and another suffered slight burns at 25 m, the fireball diameter was taken as approximately 36 m.

16.16.2 Experimental studies

The experimental studies of main relevance here are the relatively large-scale tests done by Jarrett (1952) on fireballs from solid propellants and by Gayle and Bransford (1965) on fireballs from liquid propellants. This work is described below. There are also a number of laboratory studies such as those by Mallory (1980) and Kovar *et al.* (1982).

16.16.3 Empirical features

Fireballs from high explosives tend to be of shorter duration than those of hydrocarbons for a given mass. Further, the mass involved in accidents tends to be less. Generally, therefore, the duration time of the fireball is short. The fireball diameter also appears to be less than for the same mass of hydrocarbons. On the other hand, the fireball temperatures are appreciably higher, particularly in the early stages.

16.16.4 Fireballs of munitions

For munitions fireballs, W.E. Baker *et al.* (1983) quote the following model by Rakaczky (1975). For the diameter

$$D = 3.76\, M^{0.325} \qquad [16.16.1]$$

and for the duration time

$$t_d = 0.258\, M^{0.349} \qquad [16.16.2]$$

where D is the diameter of the fireball (m), M is the mass of chemicals (kg) and t_d is the duration time (s).

Baker *et al.* state that these relations were obtained by fitting data from the literature, but no limits of applicability are given and the equations should be used with caution.

16.16.5 Fireballs of solid propellants

An investigation of the fireball from solid propellants has been described by Jarrett (1952). The work was done in connection with the storage of explosives. Its purpose was to determine the maximum extent of flame travel at ground level when a store of propellant explodes. Experiments were conducted with quantities of cordite in the range 50–175 000 lb.

For the flame radius at ground level, correlations were obtained which may be written as

$$D = 0.906\, M^{0.38} \qquad \text{Peripheral ignition} \qquad [16.16.3]$$

$$D = 0.906\, M^{0.44} \qquad \text{Central ignition} \qquad [16.16.4]$$

16.16.6 Fireballs of liquid propellants

In another early study, Gayle and Bransford (1965) described an investigation of the fireballs from liquid propellants and from high explosives, based on a literature survey and measurements taken from photographs

in experimental work. The propellants considered were RP-1/LOX, LH_2/LOX, RP-1/LH_2/LOX and N_2O_4/UDMH-hydrazine (LH_2, liquid hydrogen; LOX, liquid oxygen). These liquid propellants are therefore strictly bipropellants incorporating their own oxidizer for combustion. The high explosive tests are considered further below.

Gayle and Bransford comment that the fireball diameters for the liquid propellants were governed almost exclusively by the mass involved. The diameters effectively obeyed the cube root law.

They state further that there was little difference in the diameters of the fireballs from the liquid bipropellants and from high explosives. They give separate equations for the diameter of the fireball for individual liquid bipropellants and the following equation for the combination of liquid bipropellants and high explosives:

$$d = 9.56\ W^{0.325} \qquad [16.16.5]$$

where d is the diameter of the fireball (ft) and W is the mass of material (fuel + oxidizer) (lb). In SI units

$$D = 3.77\ M^{0.325} \qquad [16.16.6]$$

The duration times of the fireballs were relatively variable. These authors attribute this partly to variations in photographic variables and partly to the difficulty of defining the end of the visible fireball in an unambiguous manner. For the combined set of liquid bipropellants they give for the duration time:

$$t_d = 0.196\ W^{0.349} \qquad [16.16.7]$$

where W is the mass of material (fuel + oxidizer) (lb). In SI units

$$t_d = 0.258\ M^{0.349} \qquad [16.16.8]$$

where M is the mass of material (fuel + oxidizer) (kg).

The duration times of the high explosive fireballs were appreciably shorter, but no correlation is given.

For liquid bipropellants, R.W. High (1968) has given the following model:

$$d = 0.82\ W^{0.320} \qquad [16.16.9]$$

$$t_d = 0.232\ W^{0.320} \qquad [16.16.10]$$

where W is the mass of bipropellant (lb). In SI units

$$D = 3.86\ M^{0.320} \qquad [16.16.11]$$

$$t_d = 0.299\ M^{0.320} \qquad [16.16.12]$$

High gives graphs showing experimental data for the diameter and duration time of a number of liquid bipropellants together with his correlation lines. The data cover the range 10–10^5 kg.

Fireballs from liquid propellants are one of the hazards reviewed in the *Hazards of Chemical Rockets and Propellants Handbook* (Jensen, 1972). The authors quote Equations 16.16.6 and 16.16.8 from the work of Gayle and Bransford and give some additional results, as described below.

They make the point that the fireball can be very asymmetrical. The Titan test with 100 000 lb of RP-1/LOX gave maximum horizontal dimensions of 800–1000 ft, whereas the equivalent diameter from Equation 16.16.5 is some 400 ft.

They describe work on fireballs in Project Pyro and quote the following equations for the duration time of experiments done with 25 000 lb of liquid bipropellants:

$$t_d = 0.113\ W^{0.333} \qquad \text{RP-1/LOX} \qquad [16.16.13]$$

$$t_d = 0.077\ W^{0.333} \qquad \text{LH}_2\text{/LOX} \qquad [16.16.14]$$

They also describe further work on fireballs of propellant ANB-3226, which has a mass fraction of 69% oxidizer and 15% aluminium, in Project Sophy and give tabulated data.

There are several points of interest in the data given. The ratio of the maximum height of the fireball to its maximum diameter is an indication of the extent to which it undergoes a transition from hemispherical to spherical shape. This ratio is in the range 1.5–2.4. In other words, in most cases the fireball grows to a nearly spherical shape. The times to maximum diameter and to maximum height, and the ratio of these to the duration time are also significant. The ratio of the time to maximum height to the time to maximum diameter is generally of the order of 3, but can vary between 1.5 and nearly 10. If the ratio of the time to maximum diameter to the duration time is considered, this tends to be small, typically in the range 0.03–0.15.

16.16.7 Fireballs of high explosives

There is relatively little in the literature by way of models for high explosive fireballs. The high explosive experiments of Gayle and Bransford (1965), mentioned earlier, consisted of some 14 explosions involving TNT, Composition C-4 and pentolite. For the fireballs from these explosions they obtained the following equation:

$$d = 8.50\ W^{0.341} \qquad [16.16.15]$$

where d is the diameter (ft) and W is the mass of explosive (lb). The quantities of explosive were in the range 3–10^6 lb. In SI units

$$D = 3.3\ M^{0.341} \qquad [16.16.16]$$

As stated above, Gayle and Bransford did not give a correlation for the duration time of a high explosive fireball. They give some limited data which indicate that for a mass of explosive of 23 kg the duration time obtained was 0.23 seconds.

Stull (1977) quotes for TNT the following model:

$$d = 0.5\ W^{0.333} \qquad [16.16.17]$$

$$t_d = 0.23\ W^{0.333} \qquad [16.16.18]$$

He gives for these correlations two separate sources: for fireball diameter, the work of van Dolah and Burgess (1968); and for the fireball duration, that of Strehlow and Baker (1975).

Not all the models quoted are original. High quotes the work of Gayle, prior to publication of the report by Gayle and Bransford, and his model, although not the same as that of the latter authors, appears to be based on some of their data. The model given by Rakaczky appears to be the one by Gayle and Bransford. The model of Stull also is very similar to that by Gayle and Bransford.

16.16.8 Fireball temperature

According to W.E. Baker *et al.* (1983), typical fireball temperatures are

Hydrocarbons	1350 K
Solid propellants	2500 K
Liquid propellants	3600 K
High explosives	5000 K

These authors suggest that the Rakaczky model is probably applicable to fireballs with temperatures of 2500 K. They also state that a temperature of 2500 K is typical of gun propellant fireballs. Gilbert, Scilly and Lees infer that Rakaczky's model applies to gun propellant rather than liquid propellant or high explosive fireballs.

The temperatures of fireballs of liquid bipropellants are discussed by R.W. High (1968). He gives as typical a temperature of 2400 K. He also quotes computed values of 2690 and 2610 K, assuming unity and estimated emissivities, respectively. The *Rocket and Propellants Handbook* (Jensen, 1972) quotes temperatures of 2300 K obtained in Project Pyro for liquid bipropellants. The temperatures given by Baker *et al.* for propellants and high explosives appear high.

16.16.9 Gilbert, Lees and Scilly model

A model for the fireball from a high explosive has been given by Gilbert, Lees and Scilly (1995d). The model is based partly on theoretical and partly on empirical considerations.

The combustion processes in the fireball pass through two stages: (1) detonation and (2) combustion of the detonation products. The first stage is very rapid.

The growth of the fireball passes through several stages: (1) expansion following detonation; (2a) growth to the maximum diameter as a hemisphere; (2b) formation of a sphere at ground level, lift-off and rise to maximum height as a sphere; and (3) persistence at this height as a sphere until cooled.

Following detonation, air is entrained in the fireball. For oxygen deficient explosives, this air provides the oxygen required for secondary combustion of the products. The air contributes to the growth of the fireball.

It is assumed in the model that the time t_c to complete combustion is equal to the time t_s for the fireball to form the maximum size hemisphere on the ground. In other words, the end of Stage 2 of the combustion processes is taken as the end of Stage 2a of the growth process.

The model consists of relations for the diameter and the duration time of the fireball and for the profile of shape and temperature with time, and has three stages. In Stage 1 the detonation reaction occurs and gives the gaseous detonation products without admixture of air. In Stage 2 the detonation products undergo complete combustion with entrained air, except that for oxygen deficient explosives some solid carbon survives, the amount being a function of the extent of the deficiency. In Stage 3 the air entrainment decreases gradually to zero and the fireball cools. The model gives the diameter of the fireball and its temperature from the end of the detonation stage onwards.

The differences in the diameters of the fireballs in the hemispherical and spherical stages are not large. The temperatures range from approximately 2000–4200 K at the end of Stage 1 to 1150–2500 K in Stage 2.

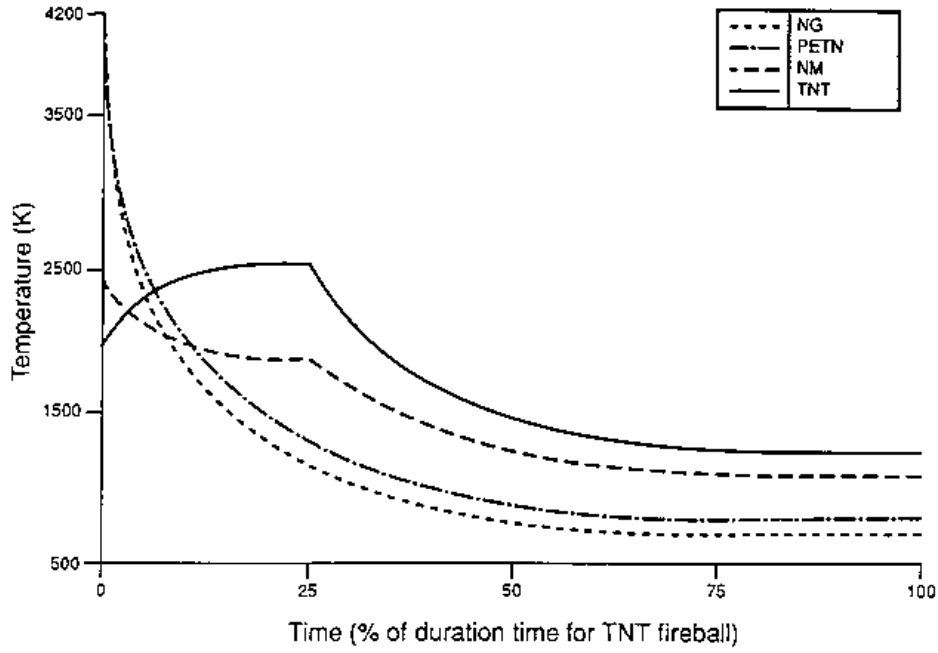


Figure 16.89 *Estimated temperatures of the fireballs of four explosives (Gilbert, Lees and Scilly, 1994e) NG, nitroglycerin; NM, nitromethane; PETN, pentaerythritol tetranitrate; TNT, trinotrotoluene*

In the overall model, the relations for the diameter and the duration time are based on the empirical models described above. The relation for the diameter is cross-checked with the heat balance model. The relations given in the model for the diameter and duration time of the fireball of a high explosive are

$$D = 3.5\, M^{0.333} \qquad [16.16.19]$$

$$t_d = 0.3\, M^{0.333} \qquad [16.16.20]$$

Equation 16.16.19 is applicable to any high explosive. Equation 16.16.20 is specific to explosives similar in oxygen balance to TNT.

For the profile of the shape and temperature the approach taken is as follows. The time required for the fireball to reach its maximum diameter is a small fraction of the total duration time. The authors define a time t_s at which the shape of the fireball changes from the maximum diameter hemisphere to a sphere, still at ground level:

$$t_s = \phi t_d \qquad [16.16.21]$$

where ϕ is a fraction. They use a value for ϕ of 0.25.

The temperature profile of the fireball is obtained from a heat balance model. In this model the detonation is taken as virtually instantaneous and the adiabatic flame temperature is determined. For an explosive which is oxygen deficient it is assumed that the rate of release of the remaining energy and the rate of entrainment of air are constant from time zero to time t_s. At time t_s combustion ceases, although air continues to be entrained at a linearly diminishing rate falling to zero at t_d. The temperature at the termination of the fireball T_f is taken as 1150 K.

The authors give for four explosives the generalized temperature profiles shown in Figure 16.89. These profiles are expressed as functions of the duration time calculated from Equation 16.16.20. This equation applies to TNT, and for this explosive the duration time is used directly. For the other explosives, an effective duration may be obtained from the graphs using a suitable value of the termination temperature T_f, taken as 1150 K.

As stated earlier, it is an implication of the values of the indices in the pair of Equations 16.16.19 and 16.16.20 that for a given explosive the temperature and thermal radiation at a given fraction of the duration time are the same for all masses of explosive.

The authors note that in the example which they give for a fireball of TNT that the fraction of heat radiated over the duration time is about 0.44.

A comparison between the diameter of the fireball in the Peterborough incident with that predicted by the model, as given in Equation 16.16.19, gives a predicted value of 33 m (spherical) or 40 m (hemispherical) compared with an apparent observed value of 36 m.

16.17 Pool Fires

A pool fire occurs when a flammable liquid spills onto the ground and is ignited. A fire in a liquid storage tank is also a form of pool fire, as is a trench fire. A pool fire may also occur on the surface of flammable liquid spilled onto water.

There is a considerable literature on pool fires, including the work of Burgoyne and Katan (1947), Rasbash, Rogowski and Stark (1956), Blinov and Khudiakov (1957), Hottel (1959), Burgess and Zabetakis (1962 BM RI 6099), Welker and Sliepecevich (1965), P.H. Thomas (1963), P.H. Thomas, Pickard and Wraight (1963), A.F. Roberts (1966, 1971b), Werthenbach (1971a, b, 1973), Yumoto (1971b), A.R. Hall (1972, 1973), de Ris and Orloff (1972), L.E. Brown, Wesson and Welker (1974a, b, 1975), Seeger (1974), Escudier (1975), Modak (1977, 1978, 1981), Raj, Moussa and Aravamudan (1979a,b), de Ris (1979), Orloff (1980), Mizner (1981), Mizner and Eyre (1982, 1983), Moorhouse (1982), Moorhouse and Pritchard (1982), Orloff and de Ris (1982), Babrauskas (1983, 1986b), Heskestad (1983a), Hirst and Eyre (1983), Considine (1984 SRD R297), Mudan (1984c), and Crocker and Napier (1986).

Some studies of pool fires are given in Table 16.63. Most work on pool fires deals with circular pools. A particular type of circular pool fire is the storage tank fire, which is considered in Section 16.17.14. A non-circular pool fire is a slot fire, which is treated in Section 16.17.15.

16.17.1 Experimental studies

There is a considerable experimental literature related to pool fires. Apart from the large number of publications on pool fires themselves, there are many relevant studies on flames such as those on combustion processes in, and heat radiation from, flames.

Much of the early work was done on relatively small diameter pool fires. Subsequent studies indicate that the effect of pool diameter is important and that it is preferable to carry out studies on large pool fires.

This initial work tended to be concerned with the determination of the liquid burning rate, of heat transfer to the liquid surface and of the fraction of heat radiated. Experimental studies on these aspects were conducted by Rasbash, Rogowski and Stark (1956) and by Blinov and Khudiakov (1957).

The work of Blinov and Khudiakov covered a wide range of pool diameters. Hottel (1959) analysed their data to show that, as the diameter of pool fire is increased, there is progression from a laminar to a transition and finally to a turbulent regime.

Burgess and Zabetakis (1962 BM RI 6099) carried out experiments on small pool fires to determine the liquid burning rate and fraction of heat radiated.

Yumoto (1971b) has done experiments to study the relative contribution of radiation and convection to heat transfer to the liquid surface in large pool fires.

Large scale tests on pool fires of LNG have been undertaken as an American Gas Association (AGA) project as described by L.E. Brown, Wesson and Welker (1975), who give correlations for the liquid burning rate and the heat radiated.

Experiments on pool fires of aviation fuels have been done by Fu (1972).

Large scale tests on pool fires of ethylene have been performed as part of the experiments done by the Ministry of International Trade and Industry (MITI), (1976) described earlier.

Table 16.63 *Some studies of pool fires*

A General	
Experimental study of pool fires, including liquid burning rate and flame height	Rasbash, Rogowski and Stark (1956); Blinov and Khudiakov (1957)
Analysis of experimental work on pool fires, including combustion regimes, heat transfer to liquid surface, liquid burning rate and flame height	Hottel (1959)
Relation for flame height	P.H. Thomas (1963)
Relation for flame tilt	Welker and Sliepcevich (1966)
Review of pool fire relations and models	Atallah and Allan (1971)
Experimental study of heat transfer to liquid surface	Yumoto (1971b)
Experimental study of pool fires	Fu (1972)
Experimental study of pool fires of LNG	May and McQueen (1973)
Theoretical study of heat radiation from pool fires, including fraction of heat radiated and relative contribution of luminous and non-luminous radiation	Sibulkin (1973)
Review of relations and models for pool fires, including liquid burning rates	Burgess and Hertzberg (1974)
Experimental study of pool fires, including liquid burning and heat radiation	L.E. Brown, Wesson and Welker (1975); Mizner (1981)
Theoretical model of a pool fire	Modak (1977)
Experimental study of pool fires, including heat transfer to liquid surface and heat radiation	Modak (1981)
Experimental study of pool fires of LPG and LNG	Mizner and Eyre (1982)
Equations for pool fires, including flame length, tilt and drag	Moorhouse (1982)
Review of relations and models for pool fires	Moorhouse and Pritchard (1982)
Review of relations and models for pool fires	Dinenno (1982)
Relation for liquid burning rate	Babrauskas (1983)
Review of relations and models for pool fires	Considine (1984 SRD R297)
Review of relations and models for pool fires	Mudan (1984c)
Theoretical model of a pool fire	Tunc and Venart (1984/85a)
Theoretical model of a pool fire	Babrauskas (1986b)
B Heat radiation	
Model of heat radiation from soot, CO_2 and H_2O in hydrocarbon flames	P.B. Taylor and Forster (1974, 1975)
Theoretical study of heat radiation from soot, CO_2 and H_2O in hydrocarbon laminar diffusion flames	Modak (1975/1979)
Model of heat radiation from hydrocarbon flames	Considine (1984 SRD R297)
C Storage tank fires	
Experimental study of heat wave in tank fires	Burgoyne and Katan (1947)
Review of relations and models for tank fires	Atallah and Allan (1971)
Experimental and theoretical study of tank fires	Werthenbach (1971a,b, 1973)
Experimental study of tank fires, including view factor	Seeger (1974)
Experimental study of fire spread between tanks	Kobori, Handa and Yumoto (1981)
Review of relations and models for tank fires, including view factor	Crocker and Napier (1986)
D Fire on spills on water	
Experimental study of spreading of LNG on water	Burgess, Murphy and Zabetakis (1970)
Theoretical model of fire on LNG spill on water	Burgess, Biordi and Zabetakis (1972)
Theoretical model of fire on LNG spill on water	Raj and Kalelkar (1973)
Theoretical model of fire on LNG spill on water	Stannard (1977)
Review of models of LNG fires, including fire on LNG spill on water, vapour cloud fire and fireballs	Schneider (1980)
Experimental study of fire on propane and LNG spills on water	Mizner and Eyre (1983)

Modak (1981) has reported experiments on pool fires of polymethylmethacrylate (PMMA). Tests on large pool fires of LPG and LNG have been described by Mizner and Eyre (1982).

There is also a number of studies of fires in storage tanks. These include the work of Burgoyne and Katan (1947), Werthenbach (1971a,b, 1973), Seeger (1974), Lois and Swithenbank (1979) and Kobori, Handa and Yumoto (1981).

Investigations have also been carried out of fires on spills of flammable liquids on water, particularly for LNG. Closely related to these are tests on the spread of liquids on water. Experimental studies of the spreading of LNG on water have been done by Burgess, Murphy and Zabetakis (1970 BM RI 7448). A model of fire on a spill of LNG has been derived from this work by Burgess, Biordi and Murphy (1972 BM PMSRC 4177).

Large scale tests of the spreading of spills and of fire on spills of LNG on water have been carried out as part of the Liquefied Gaseous Fuels (LGF) Spill Effects program by the Lawrence Livermore National Laboratory (LLNL) at the Naval Weapons Center, China Lake, California. The work has been described by Hogan, Ermak and Koopman (1981).

Other large scale tests on fire on spills of propane and LNG have been done by Shell at Maplin Sands as described by Blackmore, Eyre and Summers (1982) and Mizner and Eyre (1983).

Figure 16.90 shows a typical pool fire.

16.17.2 Empirical features

A pool fire is a complicated phenomenon and the theoretical treatment is correspondingly complex. It is appropriate, therefore, to describe first some of the empirical features of pool fires.

A pool fire burns with a flame which is often taken to be a cylinder with a height twice the pool diameter. In still air the flame is vertical, but in wind it tilts. Wind also causes the base of the flame to extend beyond the downwind edge of the pool, thus exhibiting flame drag. With some pool fires blowout can occur at a wind speed of about 5m/s.

The characteristics of a pool fire depend on the pool diameter. The liquid burning rate increases with diameter until for large diameters it reaches a fixed value. The heat radiated from the flame behaves similarly.

Some fuels, such as LNG, burn with a relatively clear flame, while others, such as kerosene and LPG, give a smoky flame. The extent of the smoke affects the heat radiation. The effect on the flame of different fuels is shown in Plates 10 and 11.

The fraction of heat radiated by a pool fire usually lies in the range 0.2–0.4. A few fuels do not burn stably but at a certain temperature exhibit boilover.

16.17.3 Modelling of pool fires

The modelling of pool fires covers the following aspects: (1) flame geometry, (2) liquid burning rate, (3) flame characteristics, (4) heat radiated and (5) view factor.

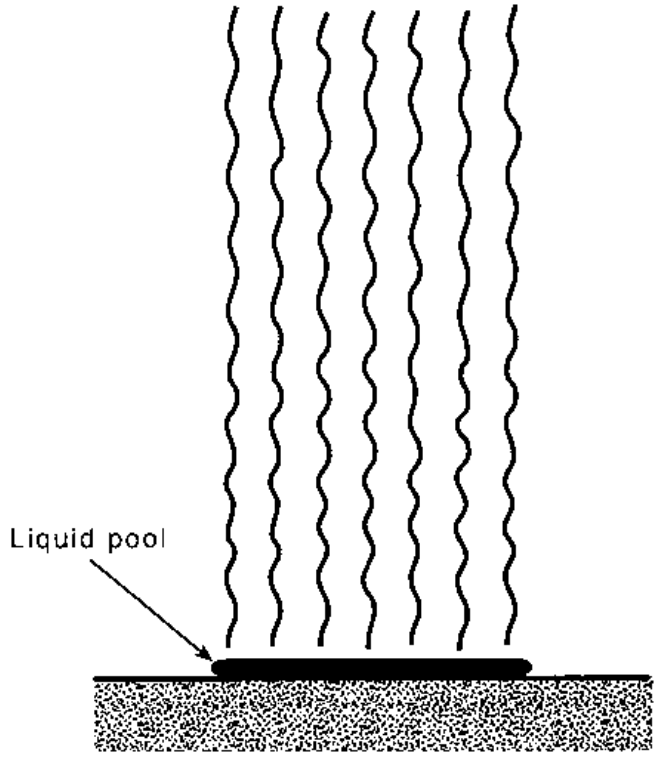


Figure 16.90 *A typical pool fire*

The approach to modelling the heat radiated from a pool fire is broadly similar to that taken for fireballs. Again, there are three different ways of determining the heat radiated: (1) the use of a value of the fraction of the heat radiated; (2) the use of a value for the surface emissivity; and (3) the estimation from the flame properties such as flame temperature and emissivity.

Reviews of pool fire models have been given by several authors, including de Ris (1979), Considine (1984 SRD R297), Mudan (1984c) and Crocker and Napier (1986).

16.17.4 Fire regimes

As just mentioned, Hottel (1958) analysed the work of Blinov and Khudiakov and showed that as the pan diameter increases the fire regime changes from laminar to turbulent. He gave the graph shown in Figure 16.91, in which burning velocity and flame height are plotted against pan diameter.

He defined a Reynolds number based on the vapour phase and related it to the parameters of the liquid phase as follows:

$$\mathrm{Re} = \frac{u_g d \rho_g}{\mu_g} \qquad [16.17.1a]$$

$$= \frac{u_l d \rho_l}{\mu_g} \qquad [16.17.1b]$$

where d is the pan diameter, u is the velocity, μ is the viscosity, ρ is the density and subscripts g and l refer to the vapour and liquid phases, respectively. The vapour phase Reynolds number was calculated using the cold gas values. The liquid velocity u_l is the liquid burning velocity v. Since the Reynolds number is proportional to the product vd, the lines of constant Reynolds number lie across the plot in Figure 16.91 from top left to bottom right with a slope of -1, as shown.

At a Reynolds number of about 20 the regime is laminar and the burning velocity decreases with increasing pan diameter. In the transition regime between Reynolds numbers of 20 and 200, the burning velocity first decreases, then increases and finally levels off with increase in pan diameter. Above Reynolds numbers of 500 the regime is turbulent and the burning velocity remains constant with increasing pan diameter. The pan diameter at which the regime becomes turbulent is about 1 m.

The flame height decreases with increasing pan diameter in the laminar and transition regimes and then remains constant with pan diameter in the turbulent regime.

16.17.5 Flame geometry

The flame on a pool fire has often been assumed to be an upright cylinder, as shown in Figure 16.90, with a length L twice the diameter D. An L/D ratio of 2 is used, for example, by Hearfield (1970) and R.B. Robertson (1976b). The work of Blinov and Khudiakov (1957) described above and shown in Figure 16.91 includes measurements of this ratio. It can be seen that for large diameters the value obtained is approximately 2.

Alternatively, the flame may be assumed to have a conical shape, but this assumption is less common and, unless otherwise stated, it is assumed in the following that the flame is treated as a cylinder.

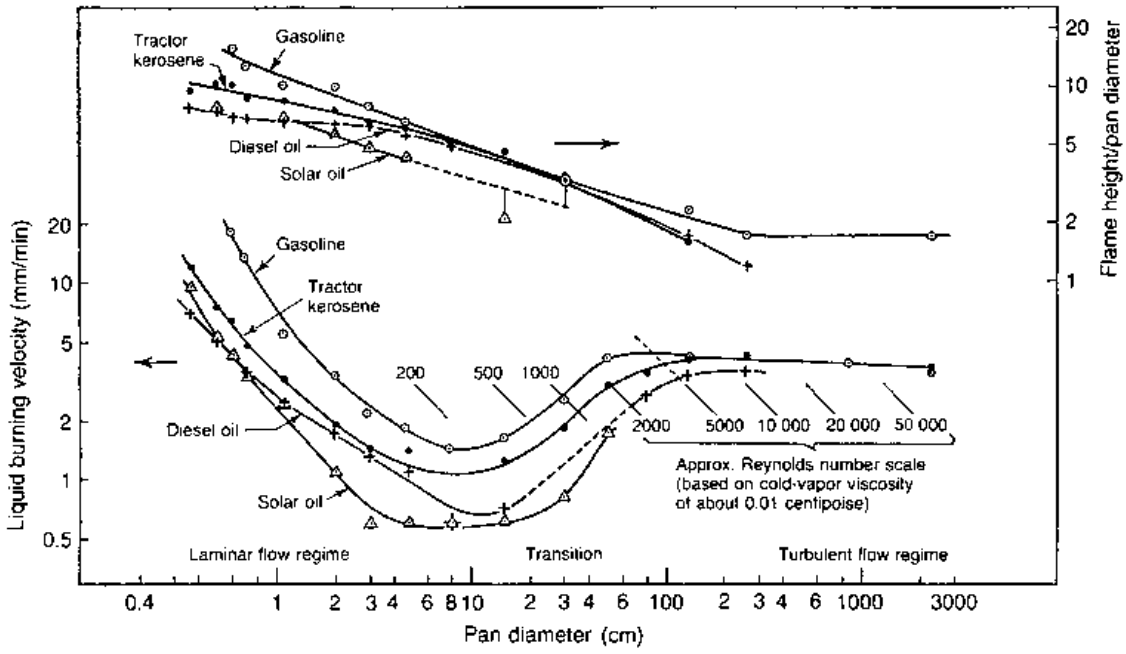


Figure 16.91 *Liquid burning rate and flame height as function of fire regime in pool fires (after Hottel, 1958; reproduced with permission)*

An equation for flame length in still air has been given by P.H. Thomas (1963). This is

$$\frac{L}{D} = 42\left[\frac{m}{\rho_a (gD)^{\frac{1}{2}}}\right]^{0.6} \qquad [16.17.2]$$

where D is the flame diameter (m), g is the acceleration due to gravity (m/s^2), L is the flame height (m), m is the mass burning rate (kg/m^2 s) and ρ_a the density of the ambient air (kg/m^3). Equation 16.17.2 is based on experiments on wood crib fires.

Steward (1970) has given a similar equation which takes into account the properties of the fuel.

Another expression for flame length is that of Heskestad (1983a). The basic relation is

$$\frac{L}{D} = f(N) \qquad [16.17.3]$$

where

$$N = \left[\frac{c_p T_o}{g\rho_a^2 (\Delta H_c / r_s)^3}\right]\frac{Q^2}{D^2} \qquad [16.17.4]$$

where c_p is the specific heat of air (kJ/kg K), ΔH_c is the heat of combustion of the fuel (kJ/kg), N is a dimensionless group, Q is the total heat release rate (kW), r_s is the stoichiometric air to volatiles mass ratio, T_o is the absolute temperature of the ambient air (K) and ρ_a is the density of the ambient air (kg/m^3).

The air/volatiles ratio r_s for a fuel $C_\alpha H_\beta O_\gamma$ burning in air is

$$r_s = 137.9\frac{\alpha + \beta/4 - \gamma/2}{12\alpha + \beta + 16\gamma} \qquad [16.17.5]$$

Heskestad has shown theoretically that for large values of N

$$\frac{L}{D} \propto N^{\frac{1}{5}} \qquad [16.17.6]$$

and has correlated experimental data with the relation

$$\frac{L}{D} = -1.02 + 15.6\, N^{\frac{1}{5}} \qquad [16.17.7]$$

The flame length in storage tank fires has been studied by Werthenbach (1971a,b, 1973). He gives an analysis, the point of departure of which is the ratio of the buoyancy to the momentum forces as given by the Archimedes number Ar:

$$\mathrm{Ar} = \frac{gD}{u^2}\,\frac{\Delta\rho}{\rho} \qquad [16.17.8]$$

where g is the acceleration due to gravity (m/s^2), u is the vapour velocity (m/s), ρ is the density of the vapour (kg/m^3) and $\Delta\rho$ is the difference between the density of the vapour and that of air (kg/m^3). Werthenbach correlates his results in terms of the Froude number Fr:

$$\frac{L}{D} = A\,\mathrm{Fr}^{0.2} \qquad [16.17.9]$$

with

$$\mathrm{Fr} = \frac{u^2}{gD^2} \qquad [16.17.10]$$

where A is a constant characteristic of the fuel. Values obtained for A were 29 for methane and natural gas and 40 for propane and gasoline. The vapour velocities were of the order of 0.75–1.0 cm/s. The author comments that these values are much lower than those in burner flames and that an attempt to apply the correlation for such flames to those on pool fires may be misleading.

Wind has several effects on the flame: it causes it to tilt, alters its length and extends it along the ground on the downwind side.

P.H. Thomas (1963) has provided an equation for flame length for a tilted flame also. This is

$$\frac{L}{D} = 55\left[\frac{m}{\rho_a (gD)^{\frac{1}{2}}}\right]^{0.67} (u^*)^{-0.21} \qquad [16.17.11]$$

with

$$u^* = u/u_c \qquad [16.17.12]$$

$$u_c = \left(\frac{gmD}{\rho_a}\right)^{\frac{1}{3}} \qquad [16.17.13]$$

where u is the wind velocity (m/s), u_c is a characteristic velocity (m/s) and u^* is a dimensionless wind velocity. The basis of Equation 16.17.11 is again experiments on fires on wood cribs.

The AGA (1973) has given an equation of the same general form as Equation 16.17.11, but with different parameters:

$$\frac{L}{D} = \left[\frac{m}{\rho_a (gD)^{\frac{1}{2}}}\right]^{-0.19} (u^*)^{0.06} \qquad [16.17.14]$$

Equation 16.17.14 therefore exhibits behaviour different from that of the Thomas Equation 16.17.11.

Moorhouse (1982) has made correlations of available data which yield

$$\frac{L}{D} = 6.2\left[\frac{m}{\rho_a (gD)^{\frac{1}{2}}}\right]^{0.254} (u_{10}^*)^{-0.044} \qquad \text{Cylindrical flame} \qquad [16.17.15a]$$

$$\frac{L}{D} = 4.7\left[\frac{m}{\rho_a (gD)^{\frac{1}{2}}}\right]^{0.2104} (u_{10}^*)^{-0.1144} \qquad \text{Conical flame} \qquad [16.17.15b]$$

with

$$u_{10}^* = u_{10}/u_c \qquad [16.17.16]$$

where u_{10} is the wind speed at a height of 10 m and u_{10}^* is the dimensionless wind speed at that height. These equations are valid for wind speeds $u_{10} > u_c$, while for wind speeds $u_{10} < u_c$ the dimensionless wind speed term is taken as unity.

Considine (1984 SRD R297) gives an analysis in which it is shown that, given certain assumptions, the use of a constant fraction of heat radiated implies a constant L/D ratio.

Thomas has also provided an equation for flame tilt

$$\cos\theta = 0.7(u^*)^{-0.49} \qquad [16.17.17]$$

where θ is the angle of tilt from the vertical (rad). The basis of Equation 16.17.17 is again experiments on wood crib fires.

The AGA (1973) has given an equation of the same form

$$\cos\theta = (u^*)^{-0.5} \qquad [16.17.18]$$

This equation is based on tests on large LNG fires.

Another correlation for flame tilt is that of Welker and Sliepcevich (1965)

$$\frac{\tan\theta}{\cos\theta} = 3.2\left(\frac{Du\rho_a}{\mu_a}\right)^{0.07}\left(\frac{u^2}{Dg}\right)^{0.7}\left(\frac{\rho_g}{\rho_a}\right)^{-0.6} \qquad [16.17.19]$$

where μ_a is the viscosity of air (kg/m s), and ρ_g is the density of the fuel vapour at the normal boiling point (kg/m^3). Equation 16.17.19 is based on experiments on small pool fires.

Moorhouse (1982) has correlated the available data to obtain equations of the form given by Thomas and of that given Welker and Sliepcevich. These are, respectively,

$$\cos\theta = 0.86(u^*_{10})^{-0.250} \quad \text{Cylindrical flame} \qquad [16.17.20a]$$

$$\cos\theta = 0.87(u^*_{10})^{-0.272} \quad \text{Conical flame} \qquad [16.17.20b]$$

and

$$\frac{\tan\theta}{\cos\theta} = 1.9\left(\frac{Du\rho_a}{\mu_a}\right)^{0.050}\left(\frac{u^2}{Dg}\right)^{0.399} \quad \text{Cylindrical flame} \qquad [16.17.21a]$$

$$\frac{\tan\theta}{\cos\theta} = 3.0\left(\frac{Du\rho_a}{\mu_a}\right)^{0.011}\left(\frac{u^2}{Dg}\right)^{0.422} \quad \text{Conical flame} \qquad [16.17.21b]$$

For flame drag, Welker and Sliepcevich (1966) give the following equation

$$\frac{D'}{D} = 2.1\left(\frac{u^2}{Dg}\right)^{0.21}\left(\frac{\rho_g}{\rho_a}\right)^{0.48} \qquad [16.17.22]$$

where D' is the elongated flame base (m). The experimental basis of Equation 16.17.22 is wind tunnel tests on small pool fires.

Moorhouse (1982) has correlated the available data to obtain the equations

$$\frac{D'}{D_w} = 1.5\left(\frac{u^2}{Dg}\right)^{0.069} \quad \text{Cylindrical flame} \qquad [16.17.23a]$$

$$\frac{D'}{D_w} = 1.6\left(\frac{u^2}{Dg}\right)^{0.061} \quad \text{Conical flame} \qquad [16.17.23b]$$

where D_w is the maximum pool dimension in the direction of the wind (m).

16.17.6 Liquid burning rate

The review by Hottel (1959) of the work of Blinov and Khudiakov includes a simple analysis of the heat q transferred from the flame to the pool, which may be written as

$$q = q_c + q_r + q_{rim} \qquad [16.17.24]$$

where q_c is the heat transferred to the pool by conduction, q_r is the heat transferred by radiation and q_{rim} is the heat transferred by the pan rim. The heats transferred by convection and by radiation are

$$q_c = \frac{\pi}{4}d^2U(T_f - T_b) \qquad [16.17.25]$$

$$q_r = \frac{\pi}{4}d^2\sigma F(T_f^4 - T_b^4)[1 - \exp(-kd)] \qquad [16.17.26]$$

where d is the pool diameter, F is the view factor, k the extinction coefficient, T_b is the absolute temperature of the burning liquid surface, T_f is the absolute temperature of the flame, U is the heat transfer coefficient and σ is the Stefan–Boltzmann constant. He considers heat transfer to a gasoline pool assuming $F = 0.25$, $T_f = 1100$ K and $U = 1$ BTU/ft^2 h.

For small pans q_{rim} will be large and the liquid burning rate will be high. For large pans q_{rim} will be negligible, q_c will be constant and q_r will be dominant with large kd and hence a large and constant value of the term $[1 - \exp(-kd)]$. For intermediate size pans q_{rim} will again be negligible, but q_r will not be so large due to the thinness of the flame. Hence the liquid burning rate will pass through a minimum for intermediate pan diameters. This analysis agrees with the experimental results shown in Figure 16.91.

An equation for the regression rate of a burning liquid surface under windless conditions has been given by Burgess and Zabetakis (1962 BM RI 6099) as follows:

$$v = v_\infty[1 - \exp(-k_1 d)] \qquad [16.17.27]$$

$$v_\infty = k_2\left(\frac{-\Delta H_c}{\Delta H_v}\right) \qquad [16.17.28]$$

where d is the diameter of the pool (cm), ΔH_c is the net heat of combustion (negative) (kJ/kmol), ΔH_v is the total heat of vaporization (kJ/kmol), v is the liquid burning rate (cm/min), v_∞ is the liquid burning rate for a pool of infinite diameter (cm/min), and k_1, k_2 are constants ($k_2 = 0.0076$).

Liquid burning rate parameters for Equation 16.17.27 for selected substances are given in Table 16.64. For LNG the maximum liquid burning rate given in Table 16.64 is 0.66 cm/min, but in further experimental work at Bruceton and Lake Charles described by these authors considerably higher values were obtained. In one experiment the burning rate was 1.16 cm/min.

Table 16.64 *Parameters for liquid burning rate on pools of selected substances (Burgess and Zabetakis, 1962 BM RI 6099) (Courtesy of the Bureau of Mines)*

	ν_∞ (cm/min)	k_1 (cm^{-1})
Hydrogen	1.4[a]	0.07[a]
Butane	0.79	0.027
Hexane	0.73	0.019
Benzene	0.60	0.026
Methanol	0.17	0.046
LNG	0.66[b]	0.03[b]

[a] Uncertain value.
[b] Value calculated.

Equation 16.17.27 also be written in the form

$$m = m_\infty[1 - \exp(-k_1 d)] \quad [16.17.29]$$

$$m_\infty = v_\infty \rho_l \quad [16.17.30]$$

where m is the mass liquid burning rate (kg/m^2 s), m_∞ is the mass burning rate for a pool of infinite diameter (kg/m^2 s) and ρ_l the liquid density (kg/m^3).

Brown, Wesson and Welker used Equation 16.17.29 to correlate the mass burning rate for large LNG fires in the AGA tests. In British Units they give for the parameters m_∞ a value of 0.6 (in./min) and k_1 a value of 0.2 (ft^{-1}).

Work on the heat transfer from the flame to the liquid pool has been reviewed by Yumoto (1971b). This work was limited to small scale fires. He describes experimental work on fires in pools up to 3 m diameter in which measurements were made of the relative contribution of convective and radiant heat transfer. As shown in Figure 16.92 the contribution of convection falls and that of radiation rises as the pool diameter increases, until both contributions reach a constant value.

Sibulkin (1973) discusses the ratio q_r/q_c. He assumes in his analysis that q_c is constant and that

$$q_r \propto \epsilon \quad [16.17.31]$$

where ϵ is the flame emissivity. He gives for the latter

$$\epsilon = 1 - \exp(-k_3 L_m) \quad [16.17.32]$$

where L_m is the mean beam length and k_3 is a constant. But for pools of intermediate diameter

$$\epsilon \propto L_m^{\frac{1}{2}} \quad [16.17.33]$$

$$L_m \propto D \quad [16.17.34]$$

Hence

$$\epsilon \propto D^{\frac{1}{2}} \quad [16.17.35]$$

$$\frac{q_r}{q_c} \propto D^{\frac{1}{2}} \quad [16.17.36]$$

For large diameter pools $\epsilon = 1$, and hence

$$\frac{q_r}{q_c} \propto \text{Constant} \quad [16.17.37]$$

An extensive review of liquid burning rates is given by A.R. Hall (1973), who considers among other things the effects of (1) the fuel, (2) fuel mixtures, (3) fuel containing dispersed water, (4) the liquid surface temperature, (5) the liquid temperature distribution, (6) the pool diameter, (7) the heat transfer from the flame to the liquid and (8) the wind speed.

Work on the burning rates of fuels of solid plastics has been reviewed by de Ris (1979) in the context of pool fires. He tabulated for the fuels including polymethylmethacrylate (PMMA), polypropylene (PP) and polystyrene (PS) a large number of potentially relevant variables and found that the actual volumetric heat release rate appears to be independent of the fuel. He explained this by the fact that the heat released per unit mass of oxygen consumed is essentially the same for most organic fuels, despite incomplete combustion, whilst the rate of oxygen consumption is controlled by the overall rate of turbulent mixing, which is driven by temperature differences that are generally insensitive to the fuel.

Babrauskas (1983, 1986b) distinguishes the following burning modes of pool fires:

Pool diameter (m)	*Burning mode*
<0.05	Convective, laminar
<0.2	Convective, turbulent
0.2–1.0	Radiative, optically thin
>1.0	Radiative, optically thick

and uses the relations

$$m = m_\infty[1 - \exp(-k\beta D)] \quad [16.17.38]$$

with

$$m_\infty = \frac{\sigma T_f^4}{\Delta h_g} \quad [16.17.39]$$

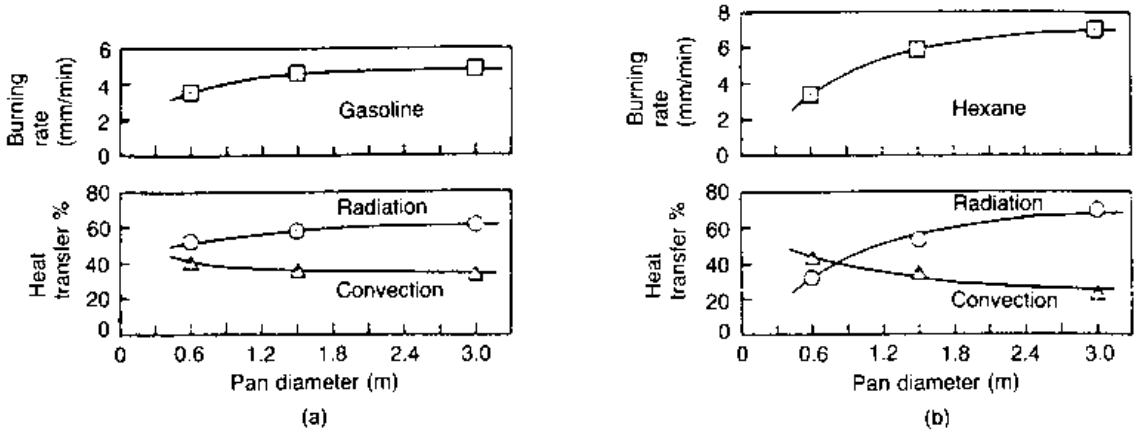


Figure 16.92 *Liquid burning rate and heat transfer to the liquid surface in large pool fires (after Yumoto, 1971b): (a) gasoline fire; (b) hexane fire (Courtesy of* Combustion and Flame*)*

Table 16.65 *Pool fire parameters for selected substances (after Babrauskas, 1983) (Courtesy of Fire Technology)*

Material	ρ_l (kg/m^3)	m_∞ (kg/m^2 s)	kβ (m^{-1})	χ_r
H_2 (liquid)	700	0.169	6.1	0.25
LNG (mostly CH_4)	415	0.078	1.1	0.16–0.23
LPG (mostly C_3H_6)	585	0.099	1.4	0.26
Butane	573	0.078	2.7	0.27–0.30
Hexane	650	0.074	1.9	0.20–0.40
Heptane	675	0.101	1.1	
Methanol	796	0.017		0.17–0.20
Ethanol	794	0.015		0.20
Benzene	874	0.085	2.7	0.14–0.38
Xylenes	870	0.090	1.4	
Acetone	791	0.041	1.9	
Diethyl ether	714	0.085	0.7	
Gasoline	740	0.055	2.1	0.18
Kerosene	820	0.039	3.5	
JP-4	760	0.051	3.6	0.35
JP-5	810	0.054	1.6	
Transformer oil (hydrocarbon)	760	0.039	0.7	
Fuel oil (heavy)	940–1000	0.035	1.7	
Crude oil	830–880	0.022–0.045	2.8	0.18

where Δh_g is the total heat of gasification (kJ/kg), k is an absorption–extinction coefficient (m^{-1}), T_f is the absolute temperature of the effective equivalent gray gas (K) and β is a mean beam length corrector. He discusses whether the mean beam length corrector β can be derived, and concludes that it cannot. He gives tabulations of m_∞ and ($k\beta$) from work on large pool fires reported by some 20 authors. These data are given in Table 16.65.

Babrauskas (1986b) also addresses some of the factors affecting the liquid burning rate, including (1) pool diameter, (2) lip effects, and (3) wind speed.

For very large pool fires with diameters greater than 5–10 m, there is some evidence of a slight decrease in burning rate. This is presumably due to poor mixing with air. Babruaskas suggests that this effect is unlikely to reduce the burning rate by more than 20%.

Effects of lip, or freeboard, on large pool fires involve all three modes of heat transfer. A lip can affect the temperature distribution in the wall of a storage tank and hence heat transfer by conduction. It can promote turbulence and enhance heat transfer by convection. It tends to make the flame more stable and emissive, thus increasing heat transfer by radiation. Babrauskas quotes the following work of Orloff (1981), on fires of one fuel, PMMA, on the effect of the ratio d/D of the freeboard height to the pool diameter on the ratio ϕ_{br} of the liquid burning rate to it base value with no lip:

d/D	ϕ_{br}
0	1.0
0.07	1.6
0.2	2.0
>0.2	Slow decrease

With regard to wind speed there is some work showing an increase in burning rate and other work indicating a decrease. Relevant studies include those of Blinov and Khudiakov (1957) and Lois and Swithenbank (1978).

Some spot values of the liquid burning rate are as follows. In the experiments of Blinov and Khudiakov on gasoline, kerosene, diesel oil and solar oil, the liquid burning rate in the turbulent regime was 0.5 cm/min. In one of the large scale tests on the pool burning of ethylene conducted by MITI (1976) a liquid burning rate of 0.88 cm/min was obtained. Values of liquid burning rate are given in the ICI *LFG Code* (ICI/RoSPA 1970 IS/74) and by Hearfield (1970) and R.B. Robertson (1976b) and liquid burning rate is treated in Chapter 22 in relation to heat radiation from fires to storage tanks.

A liquid burning rate of 0.75–1.0 cm/min is quoted in the fourth edition of the Dow *Guide* (Dow Chemical Company, 1976). This value is given in relation to the fireproofing of structures as part of the 'Recommended Minimum Fire Prevention and Protection Features', which do not appear as such in later editions.

16.17.7. Flame characteristics

Important characteristics of the flame on a pool fire are the nature of the flame, its temperature and its emissivity.

Some flammable liquids burn with a relatively clear flame, while others give a more smoky flame. The difference is well illustrated by the work of Mizner and Eyre (1982) on LNG and LPG pool fires. The LPG flames were smoky, the LNG flames much less so. Figure 16.93 illustrates the difference as do Plates 10 and 11. The presence of carbon particles in the flames has several effects. One is that the soot enhances the emissivity of the flame. Another is that smoke may shroud the flame from the target.

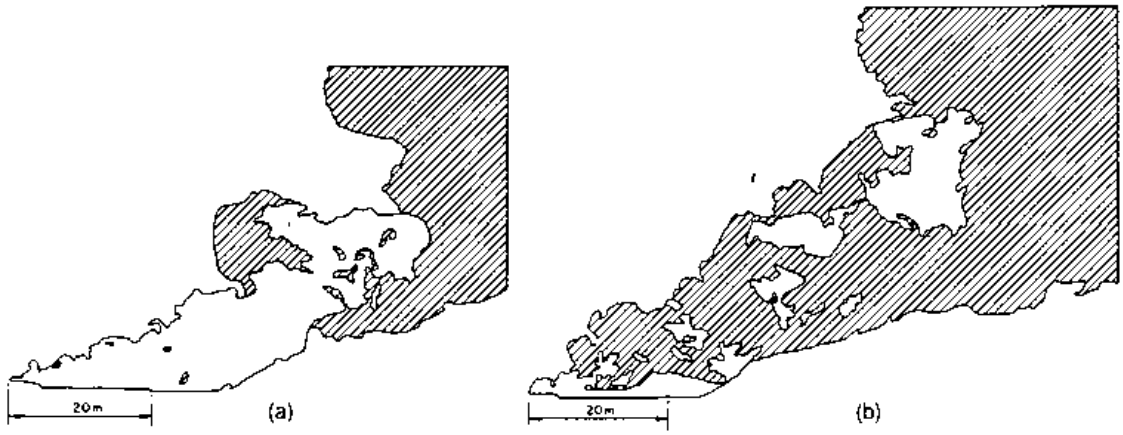


Figure 16.93 *Smokiness of flames in large pool fires (after Mizner and Eyre, 1982): (a) LNG fire; (b) LPG fire (Courtesy of the Institution of Chemical Engineers)*

Table 16.66 *Some data on the measured flame temperature and surface emissive power of flames on pool fires (Mudan, 1984c) (Courtesy of Progress in Energy and Combustion Science)*

Material	*Pool fire dimensions* (m)	*Flame radiation temperature* (K)	*Surface emissive power* (kW/m^2)	*Reference*
LNG on water	8.5–15	1500	210–280	Raj, Moussa and Aravamudan (1979b)
LNG on land	20	–	150–220	Mizner and Eyre (1982)
LPG on land	20	–	48	Mizner and Eyre (1982)
Pentane	1.0		61	Modak (1978)
Ethylene	2.5		130	Modak (1978)
Gasoline	1.0–10	1240	60–130 (max)	Hägglund and Persson (1976)
Kerosene	30–80	1600	10–25 (av.)	Japan Institute for Safety Engineering (1982)
JP-4	5.8	1200		NASA (1979)
JP-5	1.0–30		30–50	Modak (1978)

Several authors refer to a flame temperature of 1100 K. This is the typical value taken by Hottel (1959). Craven (1976) also mentions this figure, but states that this is not necessarily the maximum value which may be attained. Some data on pool fire flame temperatures given by Babrauskas are shown in Table 16.65 and further data on flame temperature and surface emissive power given by Mudan (1984c) are shown in Table 16.66. Further information on flame temperatures is given in relation to engulfing fires in Section 16.20.

As far as emissivity is concerned, pool fires of most hydrocarbon fuels become optically thick when the diameter reaches about 3 m. For such fires it is often stated that the emissivity of the flame may be taken as unity. More refined estimates of flame emissivity may be made using the relations given in Section 16.13.

The conditions which give rise to smokiness in the flame are also given in Section 16.13. If the flame is smoky, the unobscured parts of the flame will emit radiation to the target, while the obscured parts will not.

A method of taking account of obscuration of the flame has been given by Considine (1984 SRD R297). He divides the flame into unobscured sections with a surface emissive power q and obscured sections with 'blooms' of radiation where the average emissive power is $0.3q$. From photographs of flames the relative proportion of unobscured flame varied from about 30% for fires a few metres in diameter to zero for flames 50 m or more in diameter. He analyses the following three cases:

(1) flame radiating continuously over entire height;
(2) flame radiating 30% continuously, 70% in blooms;
(3) flame radiating in blooms over entire height.

He suggests that for flames in the range 5–25 m diameter the bottom 30% be taken as radiating continuously and the rest radiating in blooms, and that flames >25 m diameter be taken as radiating in blooms over their entire height. The view factor for such a flame is considered below.

16.17.8 Heat radiated

There are three methods of estimating the heat radiated by a pool fire. These are based on:

(1) heat evolved and radiated;
(2) surface emissive power;
(3) flame temperature and emissivity.

The heat evolved in the flame may be determined from the liquid burning rate. The heat radiated from the flame is then usually calculated as a fraction of the heat evolved by using an empirical factor. Some data on this radiant heat factor have been given by Burgess and Zabetakis in the work already described and are shown in Table 16.67. They suggest that the fraction of heated radiated generally does not exceed half that evolved.

It is stated by Roberts that the fraction of heat radiated both by fireballs and pool fires is typically in the range 0.2–0.4. He suggests a value of 0.3 for this radiant heat factor.

Large pool fires are affected by smoke blockage. The following data of Hägglund and Persson (1976) for the effect of pool diameter on the fraction of heat radiated in JP-4 fuel fires is quoted by Babrauskas:

Pool diameter (m)	*Fraction of heat radiated*
1.0	0.35
1.5	0.39
2.0	0.34
3.0	0.31
5.0	0.16
10.0	0.10

He states, however, that similar information is not available for other fuels and suggests that a conservative estimate can be obtained by disregarding smoke blockage. The intensity of heat radiation may then be calculated by dividing the heat radiated by the area of the flame envelope.

The second method is to use directly information on the heat radiation intensity, or emissive power, of the flame surface. Values of surface emissive power of hydrocarbon fires have been reviewed by P. Nash (1974a). He lists values of heat fluxes, extrapolated from experimental fires of different sizes, in the range 30–189 kW/m^2.

Table 16.67 *Fraction of heat radiated from flames burning on liquid pools (Burgess and Zabetakis, 1962 BM RI 6099) (Courtesy of the Bureau of Mines)*

	Pool diameter (cm)	*Heat radiated* (fraction)
Hydrogen	33	0.25
Butane	76	0.27
Benzene	122	0.36
Methanol	122	0.17
LNG	76	0.23

In the context of safety distances, a value of 170 kW/m^2 has been suggested by Law (1969). This aspect has also been discussed by Craven (1976), who concludes that the value of 170 kW/m^2 given by Law provides a realistic initial estimate.

Further data on surface emissive power are given by Mudan (1984c). His tabulated values are given in Table 16.66; he also gives other values in the text.

There are wide differences in surface emissive power, depending on the smokiness of the flame. Mizner and Eyre (1982) obtained in their work surface emissive powers of 35 kW/m^2 for kerosene, 48 kW/m^2 for LPG but 153 kW/m^2 for LNG.

Reviewing work on pool fires on land and water, Moorhouse and Pritchard (1982) conclude that for large pool fires of hydrocarbons, excluding liquefied gases, the surface emissive power is unlikely to exceed 60 kW/m^2 and state that for such fires the value of 170 kW/m^2 often quoted is based on small scale tests and is not appropriate.

With regard to pool fires of LNG, small fires clearly burn with a particularly clean flame. Evidence of soot formation is found only when the pool diameter reaches about 10 m or when most of the fuel has been consumed and the proportion of higher hydrocarbons is rising rapidly. Optical thickness is approached only when the flame is some metres wide. Moorhouse and Pritchard quote for pool fires of LNG the surface emissivities of the order of 200 kW/m^2 obtained by Raj, Moussa and Aravamudan (1979a).

Values of the surface emissive power for pool fires on water obtained in the experiments on the dispersion and burning of vapour clouds at Maplin Sands have been given by Blackmore, Eyre and Summers (1982), Hirst and Eyre (1983) and Mizner and Eyre (1983). This work has been described in Section 16.14. Pool fires formed on the liquefied gas spilled on the sea. The surface emissive power for these pool fires, as opposed to the vapour cloud fire, were 203 kW/m^2 for LNG and 43 kW/m^2 for propane. The authors suggest a value of 200 kW/m^2 as being representative for LNG pool fires.

Further indications of surface emissive power are provided in the work on engulfing fires described in Section 16.20.

L.E. Brown, Wesson and Welker (1975), in the work on LNG fires described earlier, have derived for such fires the following equation for surface emissive power:

$$q = q_\infty[1 - \exp(k_4 d)] \qquad [16.17.40]$$

where d is the diameter of the fire (ft), q is the heat flux from the surface (BTu/h ft^2), q_∞ the heat flux from the surface of a 'large' fire (BTU/h ft^2) and k_4 a constant (ft^{-1}). The values given for the parameter q_∞ is and the constant k_4 are 45 000 and 0.055, respectively.

Mudan (1984c) suggests that for hazard assessment the surface emissive power be taken as a weighted value for the unobscured and obscured portions of the flame. For example, for a flame comprising 20% luminous spots and with 80% obscured by smoke

$$q = 0.2 \times 130 + 0.8 \times 20 = 42 \text{ kW/m}^2$$

Similarly, Considine (1984 SRD R297) proposes that for hydrocarbons, but not LNG, the surface emissive power of the flame be taken as 120 kW/m^2 over the part

radiating continuously and as $0.3 \times 120 = 36\,\text{kW/m}^2$ over the part radiating in blooms.

A further discussion of the intensity of heat radiation is given in the ICI *LFG Code* and is described in Chapter 22 in relation to heat radiation from fires to storage vessels.

The third method is to determine the heat radiated from the temperature and emissivity of the flame. The heat radiated is

$$E = \epsilon\sigma T_f^4 \qquad [16.17.41]$$

where E is the surface emissive power (kW/m^2). The heat so radiated may be assumed to come either from a point source or from the flame surface. The estimation of the emissivity ϵ is discussed in Section 16.13.

In order to determine the heat incident on a target it is necessary to take into account the target absorptivity, the atmospheric transmissivity and the view factor. The determination of the latter is now considered.

16.17.9 View factor

The targets for heat radiated from a pool fire include both the liquid surface and objects outside the flame. There are therefore two different types of view factor relevant to relevant to pool fires.

As mentioned earlier, Hottel (1959) has used for the view factor of the liquid pool a value of 0.25.

For an object outside the flame there are several different treatments. For heat radiation from a flame treated as a vertical or tilted cylinder to a target the three principal models are:

(1) point source model;
(2) solid flame model;
(3) equivalent radiator model.

These models and their application have been described by Crocker and Napier (1986).

For a point source the radiation at a surface a distance r from the source is

$$E = \frac{Q_r}{4\pi r^2} \qquad [16.17.42]$$

and the radiation incident on the target is

$$I = \alpha\tau\frac{FQ_r}{4\pi l_s^2} \qquad [16.17.43]$$

where E is the surface emissive power (kW/m^2), F is the view factor, I is the thermal radiation intensity (kW/m^2), Q_r is the heat radiated (kW), r is a surface radius (m), l_s is the slant distance between the source and the target (m), α is the absorptivity of the target and τ is the transmissivity of the atmosphere.

Then from Equations 16.17.42 and 16.17.43 for a point source with a target surface normal to the line joining it to the source, as given in Equation 16.13.100

$$F = \frac{r^2}{l_s^2} \qquad [16.17.44]$$

The expressions for vertical and horizontal targets are given by Equations 16.13.101 and 16.13.102.

The geometry of this model is shown both for pool fires and for storage tanks in Figure 16.94. This approach has been used by a number of workers (e.g. Hearfield, 1970) for pool and tank fires. The point source model is not accurate for a target close to the flame and for this situation other methods should be used.

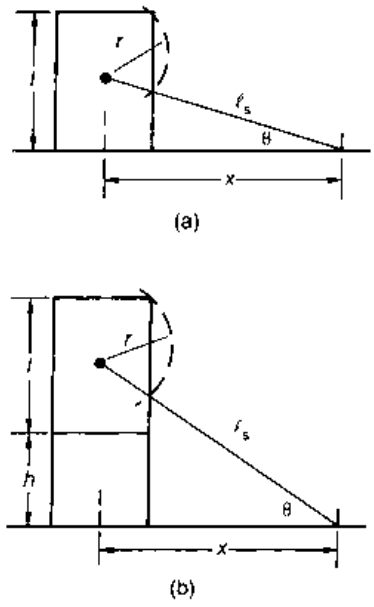


Figure 16.94 *View factor for pool and tank fires – point source model: (a) pool fire; (b) tank fire*

Of the more accurate methods, the more widely used appears to be the solid flame model. Methods for the calculation of the view factor for a vertical cylinder have been described by Hamilton and Morgan (1952) and Sparrow, Miller and Jonsson (1962), and for a tilted cylinder by Rein, Sliepcevich and Welker (1970), Merriam (1972) and Raj and Kalelkar (1974). A collection of view factors is given by Howell (1982).

For a vertical cylinder with a target with a vertical surface, as shown in Figure 16.95(a), the view factor given by Hamilton and Morgan (1952) (Howell, configuration B-29) is

$$F = \frac{1}{\pi X}\tan^{-1}\left[\frac{L}{(X^2-1)^{\frac{1}{2}}}\right] + \frac{L}{\pi}\left(\frac{(A-2X)}{X(AB)^{\frac{1}{2}}} \times \tan^{-1}\left\{\frac{[A(X-1)]^{\frac{1}{2}}}{[B(X+1)]^{\frac{1}{2}}}\right\} - \frac{1}{X}\tan^{-1}\left[\frac{(X-1)^{\frac{1}{2}}}{(X+1)^{\frac{1}{2}}}\right]\right) \qquad [16.17.45]$$

with

$$L = l/r \qquad [16.17.46a]$$

$$X = x/r \qquad [16.17.46b]$$

$$A = (X+1)^2 + L^2 \qquad [16.17.46c]$$

$$B = (X-1)^2 + L^2 \qquad [16.17.46d]$$

where r is the radius of the cylinder.

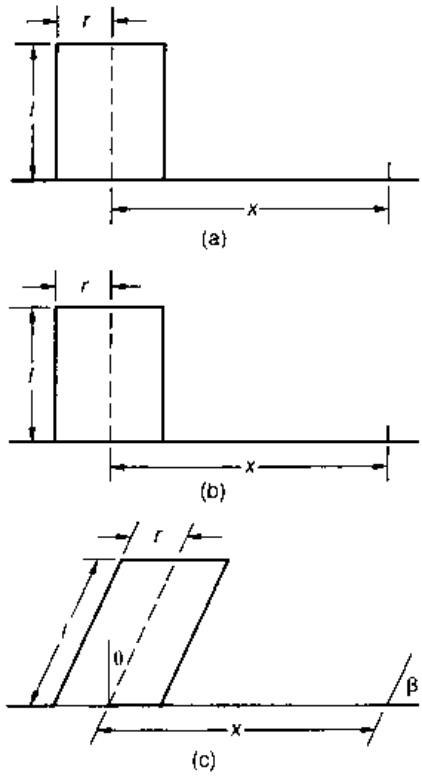


Figure 16.95 *View factor for pool fires – solid flame model: (a) vertical cylindrical flame, vertical target; (b) vertical cylindrical flame, horizontal target; (c) tilted cylindrical flame, angled target*

For a vertical cylinder with a target with a horizontal surface, as shown in Figure 16.95(b), the view factor given by Sparrow, Miller and Jonsson (1962) (Howell, configuration B-27) is

$$F = \frac{1}{2\pi}\cos^{-1}R + \frac{1}{\pi}\left\{\tan^{-1}\left[\frac{R}{(1-R^2)^{\frac{1}{2}}}\right] - \frac{(1+L^2-R^2)}{X} \times \tan^{-1}\left[\frac{X\tan(0.5\cos^{-1}R)}{1+L^2+R^2-2R}\right]\right\} \quad [16.17.47]$$

with

$$R = r/x \quad [16.17.48a]$$

$$L = l/x \quad [16.17.48b]$$

$$X = [(1+L^2+R^2)^2 - 4R^2]^{\frac{1}{2}} \quad [16.17.48c]$$

For a vertical cylinder, an expression based on the more approximate subtended solid angle method has been given by Stannard (1977)

$$F = \frac{2}{\pi}\sin^{-1}(r/x)\sin\{\tan^{-1}[l/(x-r)]\} \quad [16.17.49]$$

For a tilted cylinder with a circular base tilted at an angle θ to the horizontal and with the target having a surface at an angle β to the horizontal, as shown in Figure 16.95(c), the view factor has been given by Mudan (1984c), following work by Raj and Kalelkar (1974), and is

$$F = \frac{1}{\pi}[(\cos\beta\sin\theta - \sin\beta\cos\theta)(A_1\cos\phi + LA_2) + \cos\beta(A_3 - A_4)] \quad [16.17.50]$$

with

$$L = l/r \quad [16.17.51a]$$

$$X = x/r \quad [16.17.51b]$$

$$\phi = \sin^{-1}(1/X) \quad [16.17.51c]$$

$$A_1 = \frac{1}{B_1}\left\{\tan^{-1}\left[\frac{L-(X-1/X)\sin\theta}{B_1}\right] + \tan^{-1}\left[\frac{(X-1/X)\sin\theta}{B_1}\right]\right\} \quad [16.17.51d]$$

$$B_1 = [(X^2-1)\cos^2\theta + (1-1/X^2)\sin^2\theta]^{\frac{1}{2}} \quad [16.17.51e]$$

$$A_2 = \int_0^{\pi/2} f(v)\,\mathrm{d}v \quad [16.17.51f]$$

$$f(v) = \frac{\sin v}{(1+L^2+X^2-2XL\sin\theta) + 2(L\sin\theta - X)\sin v} \quad [16.17.51g]$$

$$A_3 = \int_0^{\pi/2} \frac{(X\sin v - 1)\,\mathrm{d}v}{(1+X^2-2X\sin v)} \quad [16.17.51h]$$

$$A_4 = \int_0^{\pi/2} \frac{(X\sin v - 1)\,\mathrm{d}v}{[(1+L^2+X^2-2L\sin\theta) + 2(L\sin\theta - X)\sin v]} \quad [16.17.51i]$$

For a tilted cylinder with a target with a vertical surface ($\beta = 90^\circ$), Equation 16.17.50 reduces to

$$F = \frac{1}{\pi}\cos\theta(A_1\cos\phi + LA_2) \quad [16.17.52]$$

Stannard has given an expression based on the subtended solid angle method for a tilted cylinder also

$$F = \frac{2}{\pi}\sin^{-1}\left[\frac{r}{r+(x-r)\cos\theta}\right] \times \left\{\sin\theta + \sin\tan^{-1}\left[\left(\frac{1}{(x-r)\cos\theta}\right) - \tan\theta\right]\right\} \quad [16.17.53]$$

The third approach is the equivalent radiator method. For a vertical cylinder the view factor has been given by Hamilton and Morgan (1952). For a target with vertical

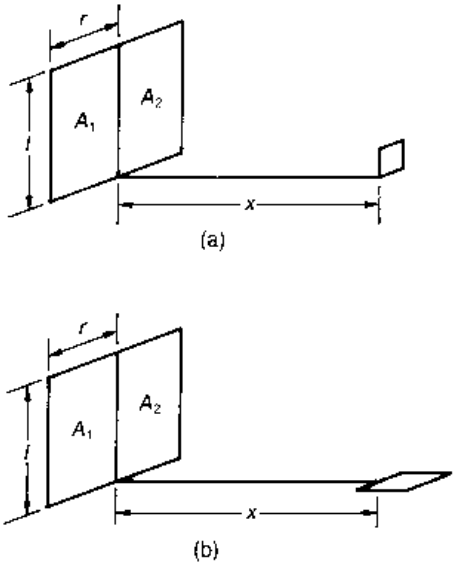


Figure 16.96 *View factor for pool fires – equivalent radiator model: (a) vertical cylindrical flame, vertical target; and (b) vertical cylindrical flame, horizontal target*

surface as shown in Figure 16.96(a) the view factor for a half-radiator is

$$F = \frac{1}{2\pi}\left\{\frac{R}{(1+R^2)^{\frac{1}{2}}}\tan^{-1}\left[\frac{L}{(1+R^2)^{\frac{1}{2}}}\right] + \frac{L}{(1+L^2)^{\frac{1}{2}}} \times \tan^{-1}\left[\frac{R}{(1+L^2)^{\frac{1}{2}}}\right]\right\} \quad [16.17.54]$$

and for a target with a horizontal surface as shown in Figure 16.96(b) the view factor for a half-radiator is

$$F = \frac{1}{2\pi}\left\{\tan^{-1}R - \frac{1}{(1+L^2)^{\frac{1}{2}}}\tan^{-1}\left[\frac{2}{(1+L^2)^{\frac{1}{2}}}\right]\right\} \quad [16.17.55]$$

with

$$R = r/x \quad [16.17.56a]$$

$$L = l/x \quad [16.17.56b]$$

Since the view factors given by Equations 16.17.54 and 16.17.55 are for half the radiator surface, they must be doubled to give the full view factors.

The maximum view factor F_m is the geometric mean of the view factor F_v for a vertical surface and the view factor F_h for a horizontal surface:

$$F_m = (F_v + F_h)^{\frac{1}{2}} \quad [16.17.57]$$

The application of the view factors just given to tank fires has been discussed by Crocker and Napier (1986). For a vertical flame and for targets with vertical surfaces three possible configurations are shown in Figure 16.97(a). Using the solid flame model for target 2 on a level with the base of the flame, the view factor for a vertical flame may be used as it is. For target 3 on a level with the centre of the flame the view factor for a vertical flame may again be used, but the value is doubled to take account of the two halves of the flame. For target 1 the view factor may be obtained as follows:

$$F = F[(l+h),x] - F[h,x] \quad [16.17.58]$$

This view factor is therefore the difference between view factors. A similar approach may be used for view factors based on the equivalent radiator model.

For a tilted flame with a target at ground level with a surface at an angle β to the horizontal, the configuration is as shown in Figure 16.97(b). Using the solid flame model given in Equation 16.17.50 the view factor is

$$F = F[(l+l'),x'] - F[l',x'] \quad [16.17.59]$$

Further expressions for more complex situations are given by Crocker and Napier.

A set of graphs for the view factors for pool fires of LPG are given in the IP *LPG Code*. Figure 16.98(a) shows a vertical cylindrical flame and Figure 16.98(b) the corresponding maximum view factor, whilst Figure 16.99(a) shows a tilted cylindrical flame and Figure 16.99(b) the maximum view factor for a cylindrical flame with an angle of tilt of 30°.

The view factor for a flame partially obscured by smoke is given by Considine (1984 SRD R297). He also gives the view factor where there is obstruction by an obstacle.

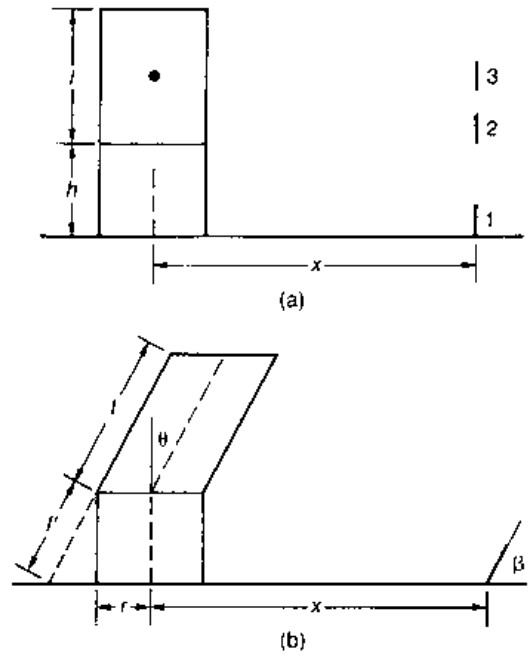


Figure 16.97 *View factor for tank fires – solid flame model: (a) vertical cylindrical flame, vertical target; and (b) tilted cylindrical flame, angled target*

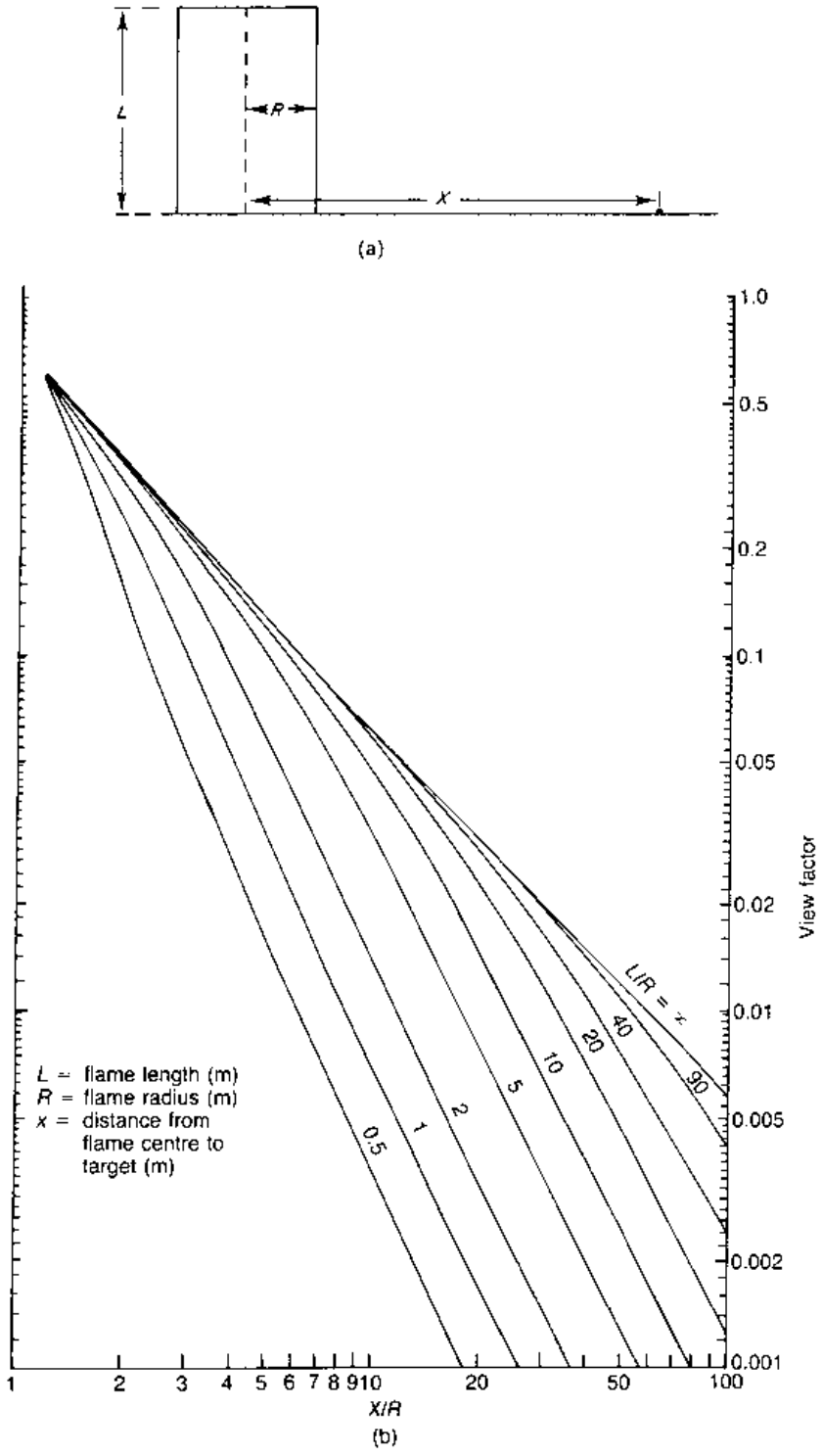


Figure 16.98 *View factor for pool fires: vertical cylinder – IP LPG Storage Code (Institute of Petroleum, 1987 MCSP Pt 9). (a) Flame; and (b) view factor (Courtesy of the Institute of Petroleum)*

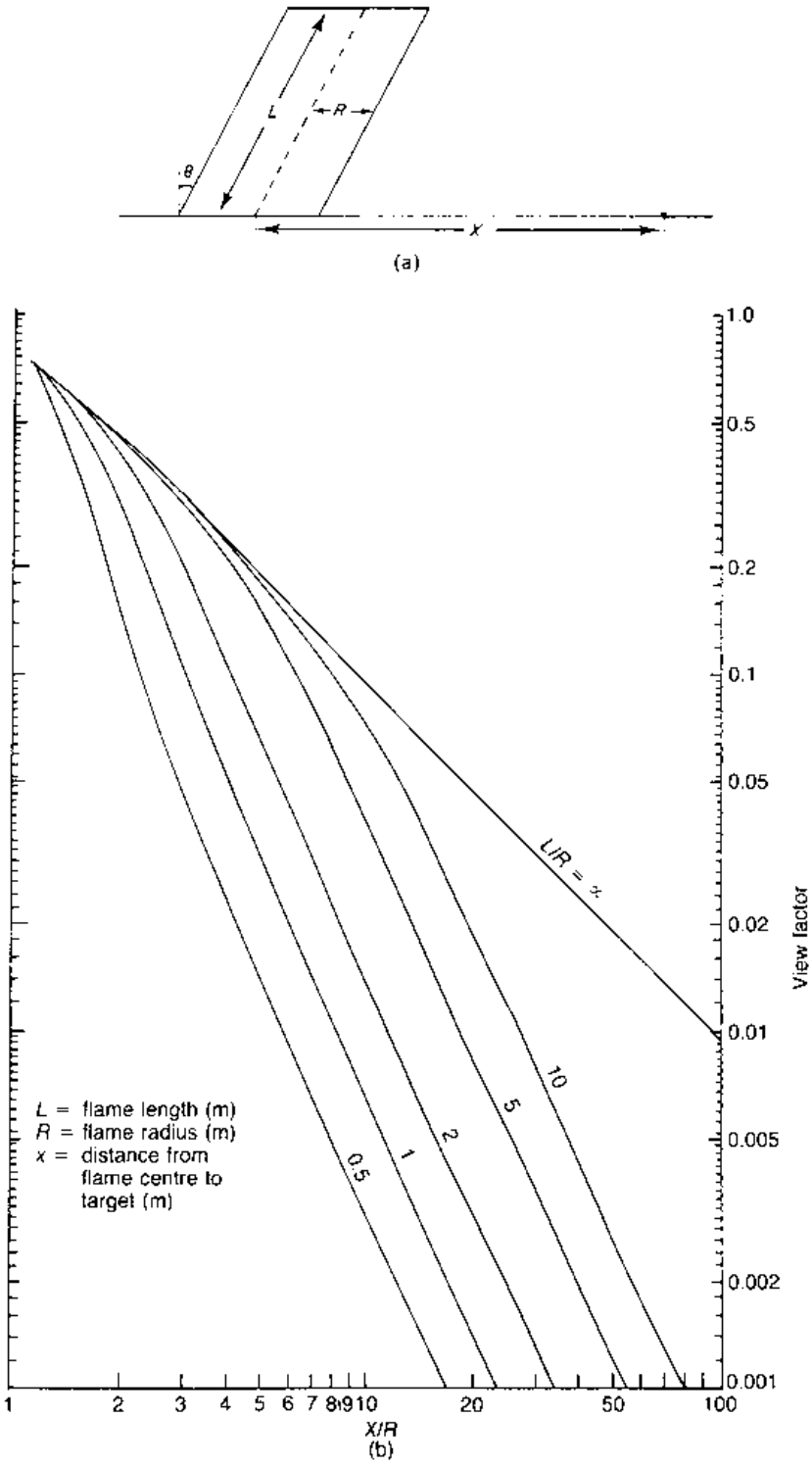


Figure 16.99 *View factor for pool fires: tilted cylinder – IP LPG Storage Code (Institute of Petroleum, 1987 MCSP Pt 9). (a) Flame; and (b) view factor. Angle of title 30° (Courtesy of the Institute of Petroleum)*

16.17.10 Pool fire models

A review of pool fire models has been given by Mudan (1984c) who describes the principal elements of pool fire models, but does not present a preferred selection. An earlier review by de Ris (1979) concentrates particularly on flame emissivity.

There are a number of models of pool fires including those by R.O. Parker (1974), Modak (1977), Mizner and Eyre (1982), Moorhouse (1982), Ndubuzu *et al.* (1983), Considine (1984 SRD R297), Tunc and Venart (1984/85a) and Babrauskas (1986b).

R.O. Parker (1974) describes a pool fire model said to give satisfactory results in accident investigation.

Modak (1977) has described a relatively complex, model consisting of a fairly large set of equations. The model is capable of determining the heat radiation to the liquid surface and to objects outside the flame. Another relatively complex model is that by Ndubuzu *et al.* (1983).

Considine (1984 SRD R297) proposes the use of the Thomas equation for flame height, the method for surface emissive power which takes account of smoke obscuration and appropriate view factors and atmospheric transmissivity. Tunc and Venart (1984/85a) have given a model of the same general type intended for the estimation of the heat radiated to a cylindrical object, such as a rail tank car, inside the flame.

Some of the other models mentioned are now described.

16.17.11 Mizner and Eyre model

Mizner and Eyre (1982) review the relations available for a pool fire. In particular, they quote for the length of flame Equation 16.17.2 and for the angle of tilt Equation 16.17.19. Their preferred values for the surface emissive power are given in Section 16.17.8.

16.17.12 Moorhouse model

The set of original correlations given by Moorhouse (1982) and Moorhouse and Pritchard (1982) constitute another pool fire model. These authors emphasize that the flame may have a conical rather than cylindrical shape. Their model contains pairs of relations, one for a cylindrical and one for a conical flame. These are: for the length of flame, Equations 16.17.15a and 16.17.15b; for the angle of tilt, Equations 16.17.20a and 16.17.20b, or Equations 16.17.21a and 16.17.21b; and for flame drag, Equations 16.17.23a and 16.17.23b. Surface emissive powers are given in Section 16.17.8.

16.17.13 Babrauskas model

Another pool fire model is that given by Babrauskas (1986b). The model uses the author's treatment of liquid burning rates described in Section 16.17.6.

With regard to flame geometry Babrauskas argues that, given the approximation involved in treating the flame as a cylinder with uniform diameter, refined methods for flame height are not justified. In his model the flame is represented as a cylinder with diameter D and height h. For a target on the ground at distance l the following quantities are defined:

$$H = h/D \qquad [16.17.60]$$

$$L = l/D \qquad [16.17.61]$$

where D is the pool diameter (m), h is the height of the flame (m) and l is the distance from its centre to the target (m). For a flame with diameter $D > 0.1\,\mathrm{m}$ it is sufficient to take $H = 1.5$.

The heat radiated by the flame is expressed in terms of the radiative power P where

$$P = \chi_r \Delta h_c m \left(\frac{\pi D^2}{4} \right) \qquad [16.17.62]$$

where Δh_c is the heat of combustion (kJ/kg), m is the mass burning rate (kg/m^{2}s), P is the radiative power (kW) and χ_r is the fraction of heat radiated.

The radiative power can also be expressed for the far field as

$$P = 4\pi l^2 q_i \qquad L > 4 \qquad [16.17.63]$$

where q_i is the thermal radiation incident on the target (kW/m^2). Hence from Equations 16.17.62 and 16.17.63

$$q_i = \frac{\chi_r \Delta h_c m}{16 L^2} \qquad L > 4 \qquad [16.17.64]$$

For the near field a more accurate estimate of the thermal radiation is

$$q_i = F \epsilon_f \sigma T_f^4 \qquad 1/2 \le L \le 4 \qquad [16.17.65]$$

where F is the view factor, T_f is the absolute flame temperature (K) and ϵ_f is the emissivity of the flame.

For the view factor F a suitable approximation is

$$F \approx H/\pi L^2 \qquad [16.17.66]$$

Then from Equations 16.17.64–16.17.66

$$\epsilon_f \sigma T_f^4 = \frac{\pi \chi_r \Delta h_c m}{16 H} \qquad [16.17.67]$$

which for $H = 1.5$ and for $D \to \infty$ reduces to

$$(\epsilon_f \sigma T_f^4)_\infty = 0.131 \chi_r \Delta h_c m_\infty \qquad [16.17.68]$$

Combining Equations 16.17.38, 16.17.64, 16.17.65 and 16.17.68 yields the relations for thermal radiation

$$q_i = \frac{\chi_r \Delta h_c m_\infty}{16 L^2} [1 - \exp(-k\beta D)] \qquad L > 4 \qquad [16.17.69]$$

$$q_i = F(0.131 \chi_r \Delta h_c) m_\infty [1 - \exp(-k\beta D)] \qquad \tfrac{1}{2} < L \le 4 \qquad [16.17.70]$$

where k is the extinction coefficient (m^{-1}) and β is the mean beam length corrector.

For the fraction of heat radiated Babrauskas refers to the data of Hägglund and Persson (1976) quoted in Table 16.65.

16.17.14 Storage tank fires

A type of pool fire which is of special interest is a storage tank fire. Such fires are usually treated as pool fires. The differences are that the liquid surface, and hence the base of the flame, is elevated and that it is surrounded by a metal wall. Another important feature is that the targets of interest usually include other storage tanks. This means that the targets may be close to the flame and that it may be necessary to consider targets at levels other than ground level and heat transfer by modes other than radiation.

Burgoyne and Katan (1947) conducted experiments on the heat wave moving through the liquid in a tank fire.

Tank fire experiments have been carried out at the Forschungsstelle für Brandschutztechnik described by Werthenbach (1971, 1971a,b, 1973) and Seeger (1974). Tank diameters up to 2 m were used. Agreement between theoretical estimates of heat radiated based on Equations 16.17.41 and 16.17.42 was obtained using a flame temperature and emissivity of 900°C and 0.9, respectively.

Seeger also investigated numerically the view factor for a vertical cylindrical flame on a tank to a target with a vertical surface on a level with the base of the flame. The effect on the view factor of altering the height of the flame or of moving the target to a level halfway up the flame was slight.

Lois and Swithenbank (1979) have used wind tunnel experiments to study fire in an array of tanks. Features considered include the effect of wind on the flame and the interaction of the wind with the tank array.

Kobori, Handa and Yumoto (1981) have studied the interactions between a tank that is on fire and a neighbouring tank that is not on fire, including heat transfer to the unignited tank by convection as well as radiation, formation of vapour in the unignited tank, induction into the fire of the vapour from that tank by the air drawn into the flame, and flashback to the unignited tank.

Crocker and Napier (1986) have reviewed the main elements of pool fire models as they apply to tank fires, have listed the applicable view factors and have considered the implications for storage tank layout.

16.17.15 Slot fires

Another type of pool fire is the slot, trench or channel fire. Such a fire may occur on a spill of flammable liquid which has entered a trench or channel of any kind. A characteristic feature is that there is a high aspect ratio. One situation in which this type of fire may occur is the burning of a liquid spill directed to a high aspect ratio catchment area.

Slot fires are discussed briefly by Moorhouse and Pritchard (1982). One approach is to treat the fire as a series of individual pool fires and then apply the relations for circular pools. This approach appears to fit the results of small scale experiments described by Welker (1965) and Gollahalli and Sullivan (1974). Further, data reported by Alger and Capener (1972) on the burning rates of large scale fires of JP-5 on a pool of aspect ratio greater than 2 are consistent with those from circular pool fires. Moorhouse (1982) states that the work on LNG pool fires which he describes included some limited tests on LNG fires with an aspect ratio of 1 to 2.5.

Work on trench fires of LNG with aspect ratios up to 30 has been conducted by Mudan and Croce (1984) and is summarized by Mudan (1989b). The work indicates that in such fires the flame height is influenced more by the width than by the length of the trench and that the flame geometry is more sensitive to wind conditions than is the case in fires on circular pools.

Mudan and Croce obtained for LNG the following correlations for flame height, angle of tilt and flame drag:

$$\frac{H}{W} = 2.2 \qquad \mathrm{Fr}' \geq 0.25 \qquad [16.17.71a]$$

$$\frac{H}{W} = 0.88\,(\mathrm{Fr}')^{-0.65} \qquad 0.1 < \mathrm{Fr}' < 0.25 \qquad [16.17.71b]$$

$$\frac{H}{W} = 4.0 \qquad \mathrm{Fr}' \leq 0.1 \qquad [16.17.71c]$$

$$\cos\theta = 0.56 \qquad \mathrm{Fr}' \geq 0.25 \qquad [16.17.72a]$$

$$\cos\theta = 0.36\,(\mathrm{Fr}')^{-0.32} \qquad 0.042 < \mathrm{Fr}' < 0.25 \qquad [16.17.72b]$$

$$\cos\theta = 1 \qquad \mathrm{Fr}' \leq 0.042 \qquad [16.17.72c]$$

$$\frac{W'}{W} = 3.5 \qquad \mathrm{Fr}' \geq 0.25 \qquad [16.17.73a]$$

$$\frac{W'}{W} = 23.3\,(\mathrm{Fr}')^{1.37} \qquad 0.1 < \mathrm{Fr}' < 0.25 \qquad [16.17.73b]$$

$$\frac{W'}{W} = 1 \qquad \mathrm{Fr}' \leq 0.1 \qquad [16.17.73c]$$

with

$$\mathrm{Fr}' = u_w/2(gW)^{\frac{1}{2}} \qquad [16.17.74]$$

where Fr′ is a modified Froude number, g is the acceleration due to gravity (m/s^2), H is the length of the flame, u_w is the wind speed (m/s), W is the width of the trench (m), W′ is the extended width of the flame base (m) and θ is the angle of tilt (°). For calm conditions, where the value of Fr′ is very low, the flame geometry depends only on the trench width. For values of Fr′ which are higher but still less than about 0.25, the flame length decreases but the angle of tilt and flame drag increase with wind speed. For still higher values of Fr′ the flame geometry is independent of wind speed. The correlations are not strictly applicable where the wind direction is parallel to the axis of the trench. The application of these relations to liquid fuels other than LNG is uncertain.

16.18 Flares

A jet flame occurs when flammable gas issuing from a pipe or other orifice is ignited and burns on the orifice. Historically, treatments of such flames have been concerned mainly with flames which are there by design, such as the flames on burners and flares. It is convenient, therefore, to start by considering flares.

The fundamentals of combustion in flares have been studied by Brzustowski and co-workers (e.g. Bzrustowski, 1973, 1977; Brzustowski and Sommer, 1973; Bzruztowski *et al.*, 1975) and by others.

16.18.1 Experimental studies

There is vast literature on flames. Discussion here is limited to some of the studies which have been concerned specifically with flare systems. Some of the studies on flares are tabulated in Section 16.19.

Conventionally, flares have been designed to give a flame which is vertical in still air. The use of flares on offshore oil production platforms, where helicopter access is necessary, has prompted the development of flares with an inclined flame. The models developed for inclined flares are relevant to jet flames arising from accidents.

A series of experimental studies of flares has been reported by Brzustowski and co-workers. The correlations obtained by Brzustowski and Sommer (1973) are the basis of the more elaborate flare model given in API RP 521, as described below.

Various workers have found that the API methods tend to overpredict the incident heat radiation. The need for tighter design of flares offshore, where space is limited, has given an incentive to obtain improved methods.

Experiments on flares have been conducted by Shell and are described by Chamberlain (1987). Ranges of some of the parameters in these trials were as follows: gas molecular weight 16–44; pipe diameter 0.006–1.07 m; Mach number 0.06–0.9; gas exit velocity 14–554 m/s; and wind speed 2.7–13 m/s. This work is the basis of the Chamberlain flare model given below.

Chamberlain's work has been extended in the model by A.D. Johnson, Brightwell and Carsley (1994), also described below. This work was on natural gas. The ranges of some of the parameters were: pipe diameter 0.02–0.152 m; gas mass flow 2.8–8.4 kg/s; and wind speed 0.3–6.9 m/s.

Other experiments have been carried out by British Gas, as described by D.K. Cook, Fairweather, Hammonds and Hughes (1987). The experiments were on natural gas and the flows were both subsonic and sonic. Ranges of some of the other parameters in these trials were as follows: pipe diameter 0.051–0.59 m; gas exit velocity 89–402 m/s; and wind speed 1.0–13 m/s.

Table 16.68 *Fraction of heat radiated by a flare*

A Fraction of heat release F_r: overall values

Gas	F	*Reference*
Methane	0.16	Brzustowksi and Sommer (1973)
Propane	0.33	Kent (1964)
Butane	0.30	Brzustowksi and Sommer (1973)
Ethylene	0.38	Brzustowksi and Sommer (1973)

B Fraction of heat release F_r: values as function of burner diameter[a]

Gas	*Burner diameter* (cm)	F_r (%)
Hydrogen	8.4	0.16
	20.3	0.15
	40.6	0.17
Butane	8.4	0.29
	20.3	0.28
	40.6	0.30
Methane	8.4	0.15
Natural gas	20.3	0.19
	40.6	0.23

[a] Zabetakis and Burgess (1961 BM RI 5707); quoted in API RPI 521: 1990. Also Burgess and Zabetakis (1962 BM RI 6099).

16.18.2 Hajeck and Ludwig model

An equation which has been widely used for the determination of the thermal radiation from a flame on a flare stack is that of Hajek and Ludwig (1960)

$$I = \frac{F_r Q}{4\pi r^2} \qquad [16.18.1]$$

where F_r is the fraction of heat released which is radiated, I is the radiation intensity on the target (kW/m^2), Q is the net heat release rate (kW) and r is the radius from the centre of the flame (m).

Combustion in the flare is a complex process. In Equation 16.18.1 this complexity is subsumed in the factor F_r. This factor has traditionally been taken as a property of the fuel only. It has been shown, however, that the F_r factor depends also on other features of the flame such as the Reynolds number. The F_r factor is discussed by Brzustowki (1977) and by Straitz *et al.* (1977). Some values of the fraction F_r of heat radiated are given in Table 16.68.

For the determination of radiation exposure, the current version of API RP 521 gives Equation 16.18.1 in the form

$$D = \left(\frac{\tau F_r Q}{4\pi K}\right)^{\frac{1}{2}} \qquad [16.18.2]$$

where D is the distance from the centre of the flame to the target (m), K is the allowable radiation (kW/m^2) and τ is the atmospheric transmissivity.

16.18.3 API RP 521 models

Flare models which have been widely used are those given in the successive editions of API RP 521 *Guide for Pressure-relieving and Depressuring Systems*. API RP 521: 1990 gives two models. The first is described as a simplified approach. The second is based on the method of Brzustowski and Sommer (1973).

The simplified model is as follows. The Mach number Ma at the flare tip is

$$\mathrm{Ma} = 11.61 \times 10^{-2} \frac{W}{Pd^2}\left(\frac{T}{kM}\right)^{\frac{1}{2}} \qquad [16.18.3]$$

where d is the flare diameter (m), k is the ratio of the specific heats of the gas, M is the molecular weight of the gas, P is the absolute pressure just inside the flare tip (kPa), T is the absolute temperature of the gas (K) and W is the mass flow of gas (kg/s).

The flare diameter is determined by setting a suitable value of the Mach number. The *Guide* gives as examples values of 0.2 and 0.5.

The length of the flame is a function of the heat release and is determined from Figure 16.100.

The distortion of the flame caused by the wind velocity is defined in terms of the horizontal deviation $\Sigma\Delta x$ and the vertical deviation $\Sigma\Delta y$ of the flame tip and is a function of the ratio of the velocity at the flare tip u_j to

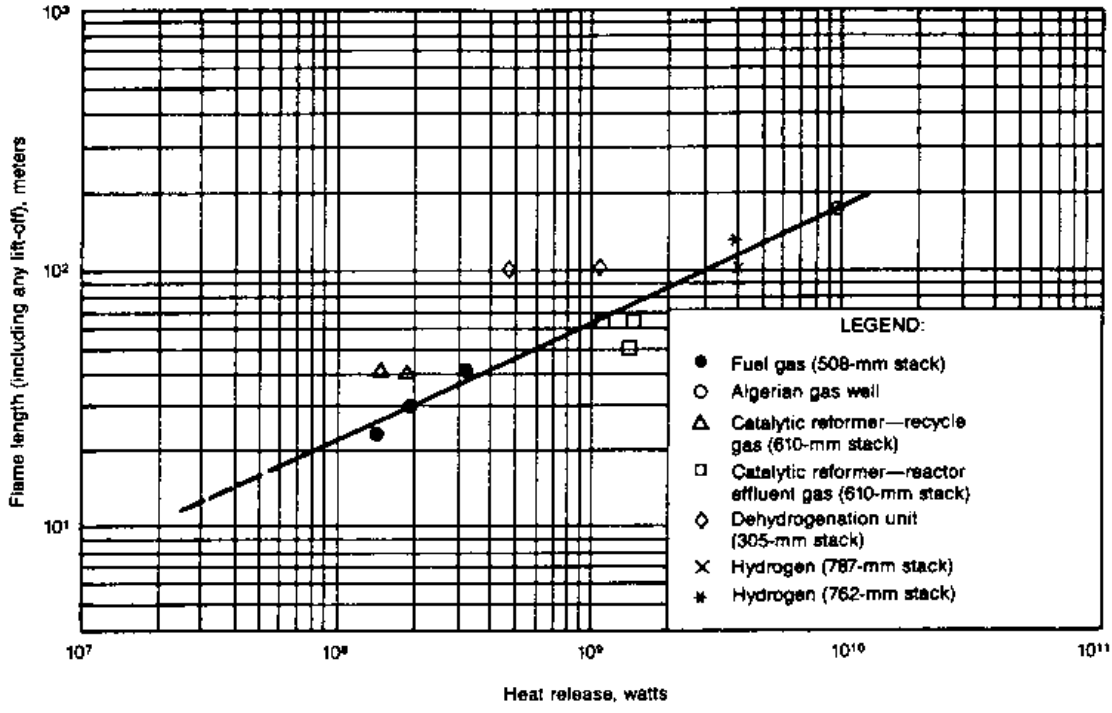


Figure 16.100 *Flare flames: flame length (API RP 521: 1990; reproduced with permission). (Multiple points indicate separate observations or different assumptions of heat content)*

the wind velocity u_∞. The flare tip exit velocity u_j is obtained as

$$u_j = \frac{V}{\pi d^2/4} \qquad [16.18.4]$$

or as

$$u_j = \mathrm{Ma}\, u_s \qquad [16.18.5]$$

with

$$u_s = 91.2\left(\frac{kT_j}{M_j}\right)^{\frac{1}{2}} \qquad [16.18.6]$$

where u_j is the exit velocity of the gas at the flare tip (m/s), u_s is the velocity of sound (m/s), u_∞ is the velocity of the wind (m/s), V is the volumetric flow of gas (m^3/s) and subscript j denotes the flare tip exit. The co-ordinates of the flame tip are determined using Figure 16.101.

This method does not give an explicit relation for the intensity of heat radiation on a target, but use may be made of Equation 16.18.2.

16.18.4 Brzustowksi and Sommer model

In the second method given in API RP 521, the Brzustowksi and Sommer model, the flare diameter is determined in the same manner by using Equation 16.18.3. The centre of the flame is then determined as follows. The horizontal distance x_c and the vertical distance y_c from the flare tip to the centre of the flame are

$$x_c = f(\bar{C}_L, d_j R) \qquad [16.18.7]$$

$$y_c = f(\bar{C}_L, d_j R) \qquad [16.18.8]$$

with

$$\bar{C}_L = C_L \frac{u_j}{u_\infty}\frac{M_j}{29} \qquad [16.18.9]$$

$$R = \frac{u_j}{u_\infty}\left(\frac{T_\infty M_j}{T_j}\right)^{\frac{1}{2}} \qquad [16.18.10]$$

where C_L is the lower explosive limit (volume fraction), R is a parameter, T_∞ is the absolute temperature of the air (K), x_c and y_c are the horizontal and vertical distances of the flame centre from the flame tip (m) and $\bar{C}_L$ is a modified lower explosive limit (volume fraction). The co-ordinates of the flame centre are determined using Figure 16.102.

Equation 16.18.2 is used to determine the intensity of heat radiation incident on a target.

16.18.5 de Faveri *et al.* model

Another flare model is that by de Faveri *et al.* (1985). These workers performed wind tunnel experiments on

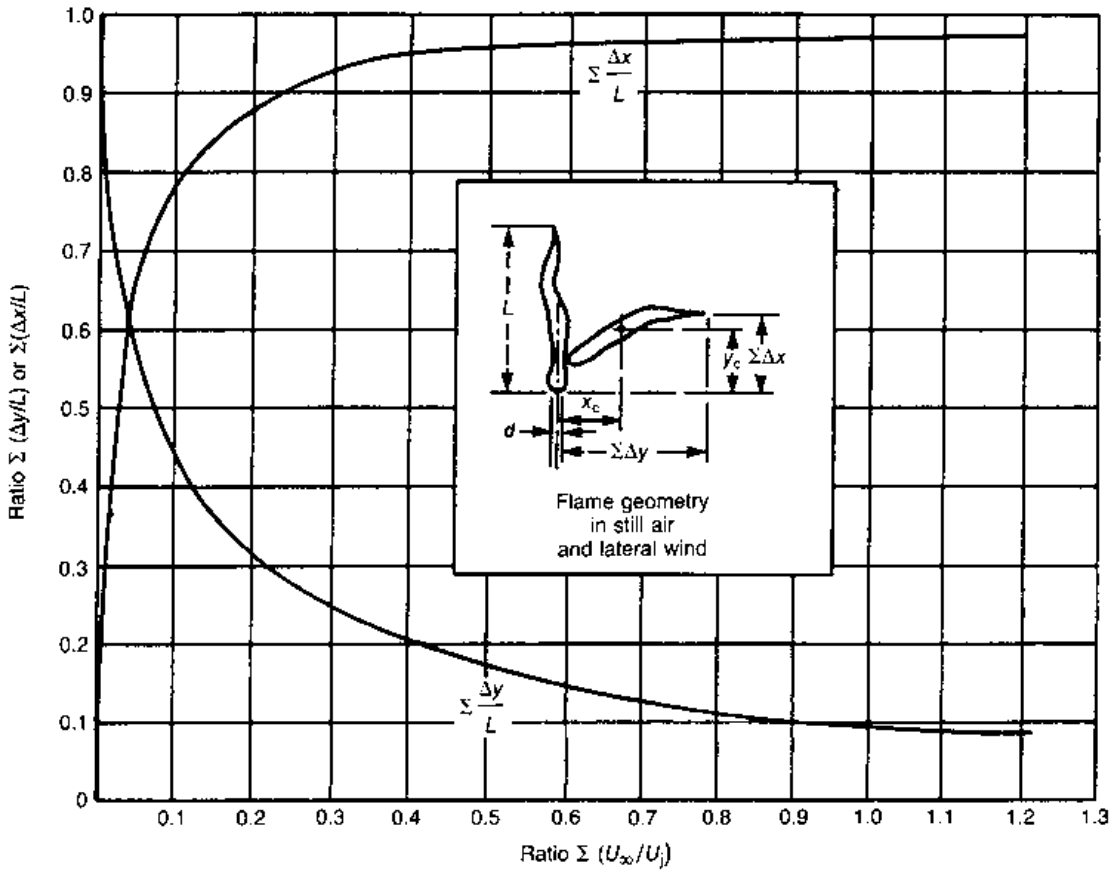


Figure 16.101 *Flare flames: distortion due to wind (API RP 521: 1990; reproduced with permission). U_∞, Lateral wind velocity; U_j exit gas velocity from the stack*

small 'flares' in a wind and obtained correlations for various features of the flare such as the downwind position of the flame tip and the axis of the flame.

This model has been discussed by Crocker and Napier (1988b) in relation to multiple point source modelling of flare radiation.

16.18.6 Chamberlain model

The flare model given by Chamberlain (1987) of Shell is based on the flame shown in Figure 16.103. The geometric components of the model are (1) the effective diameter of the source D_s, (2) the length of the flame in still air L_o, (3) the length of the flame in the pertaining conditions L, (4) the angle between the axis of the orifice and that of the flame α, (5) the lift-off distance of the frustrum of the flame b, (6) the length of the frustrum R_L, (7) the width of the base of the frustrum W_1, (8) the width of the top of the frustrum W_2 and (9) the area of the flame A.

The parameters which define the model geometry are determined as functions of the velocity ratio R

$$R = v/u_j \qquad [16.18.11]$$

where u is the gas velocity (m/s), v is the wind velocity (m/s) and subscript j denotes the expanded jet.

The model equations are as follows. As described in Chapter 15, use is made of D_s for the source. For unchoked flow

$$D_s = d_o\left(\frac{\rho_j}{\rho_a}\right)^{\frac{1}{2}} \qquad [16.18.12]$$

with

$$\rho_j = \rho_g^o \frac{273}{T_j} \qquad [16.18.13]$$

where d_o is the throat diameter of an imagined flow nozzle (m), D_s is the effective diameter of the source (m), T_j is the temperature of the gas in the expanded jet (K), ρ_a is the density of air (kg/m^3), ρ_g^o is the density of the gas under standard conditions (kg/m^3) and ρ_j is the

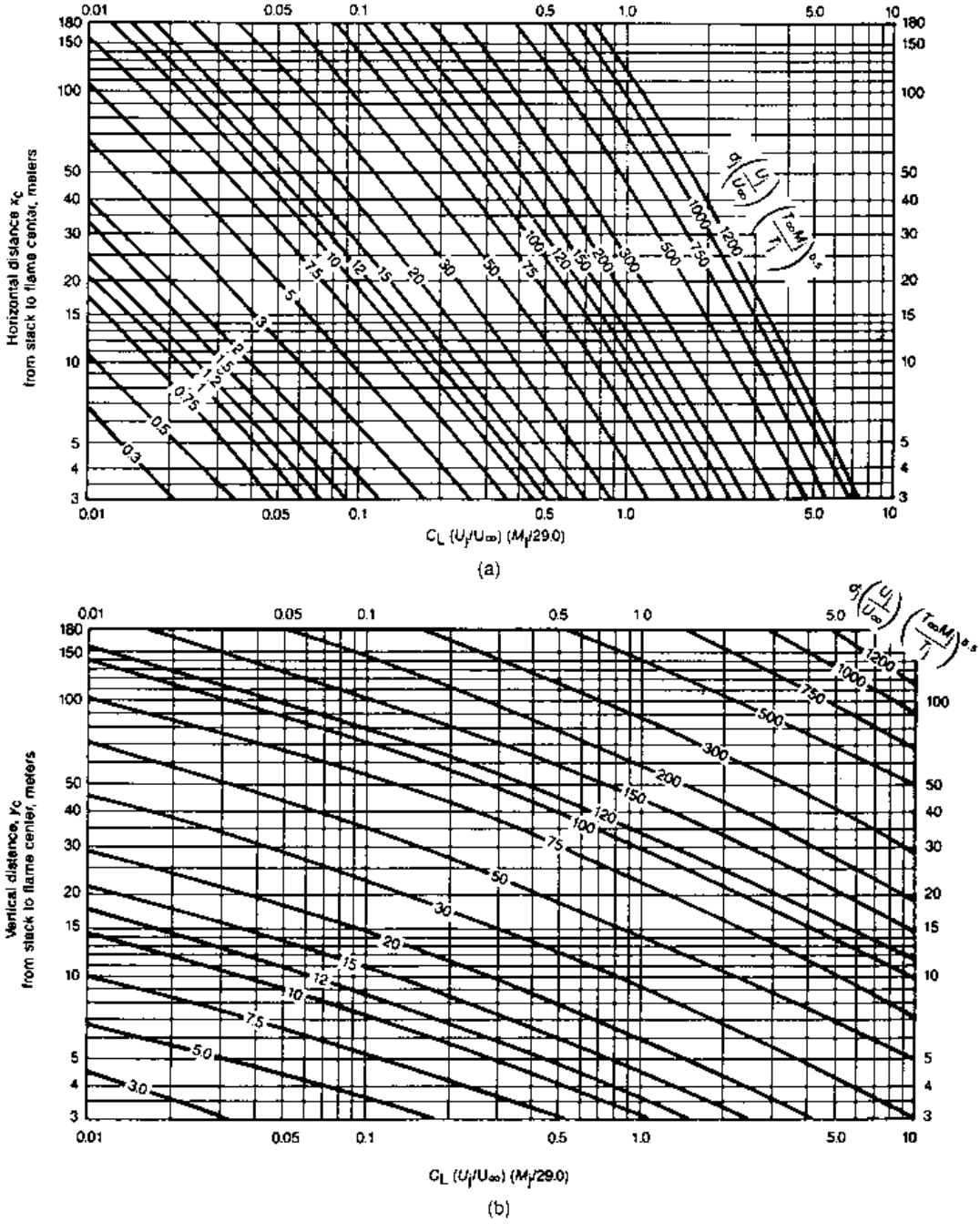


Figure 16.102 *Flare flames: location of flame centre (API RP 521: 1990; reproduced with permission). (a) Horizontal distance x_c of the flame centre from the orifice; and (b) vertical distance (m) of the flame centre from the orifice. C_L, lower explosive limit; y_c, volume fraction; d_j, inside diameter of flare tip (m); M_j, molecular weight of the gas; T_j, temperature of the gas (K); T_∞, temperature of the air (K); U_j, gas exit velocity (m/s); U_∞, average wind velocity (m/s)*

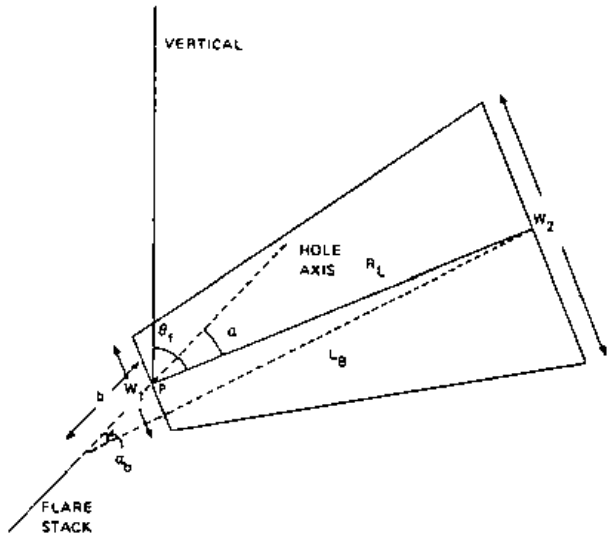


Figure 16.103 *Flare flames: flame dimensions for Chamberlain model (Chamberlain, 1987). (Note that point P is always at the intersection of the hole and frustrum axes) (Courtesy of the Institution of Chemical Engineers)*

density of the gas in the expanded jet (kg/m^3). For choked flow the jet expands to atmospheric pressure at a plane downstream of the exit hole, the plane then acting as a virtual source of diameter d_j. Then

$$D_s = d_j\left(\frac{\rho_j}{\rho_a}\right)^{\frac{1}{2}} \qquad [16.18.14]$$

with

$$d_j = \left(\frac{4\dot{m}}{\pi u_j \rho_j}\right)^{\frac{1}{2}} \qquad [16.18.15a]$$

$$= \frac{4\dot{m}}{\pi P_o \mathrm{Ma_j}}\left(\frac{R_c T_j}{\gamma M_k}\right)^{\frac{1}{2}} \qquad [16.18.15b]$$

where d_j is the diameter of the virtual source (m), $\dot{m}$ is the mass flow of gas (kg/s), M_k is the kilogram molecular weight of the gas (kg/mol), $\mathrm{Ma_j}$ is the Mach number of the expanded jet, P_o is the absolute atmospheric pressure (N/m^2), R_c is the universal gas constant (J/kmol K), u_j is the velocity of the gas in the expanded jet (m/s) and γ is the ratio of the specific heats of the gas.

For the length L_{Bo} of the flame in still air the implicit equation of Kalghatgi (1984) is used:

$$\Psi(L_{Bo}) = 0.2 + 0.024\xi(L_{Bo}) \qquad [16.18.16]$$

with

$$\Psi(L_{Bo}) = \left(\frac{D_s \beta}{L_{Bo} W}\right)^{\frac{2}{3}} \qquad [16.18.17]$$

$$\xi(L_{Bo}) = \left(\frac{g}{D_s^2 u_j^2}\right)^{\frac{1}{3}} L_{Bo} \qquad [16.18.18]$$

$$\beta = \left(\frac{M_a T_1}{M_p T_a}\right)^{\frac{1}{2}} \qquad [16.18.19]$$

where g is the acceleration due to gravity (m/s^2), L_{Bo} is the length of the flame in still air (m), M is the molecular weight of the gas, T is the absolute temperature (K), u is the velocity of gas, W is the mass fraction of the fuel in a stoichiometric mixture with air, and ξ is the Richardson number based on the flame length in still air. The subscript a denotes air, j the conditions in the expanded jet, p the mean product value and 1 adiabatic combustion conditions.

For a paraffin of molecular weight M the mass fraction W of fuel in a stoichiometric mixture with air is

$$W = \frac{M}{15.816M + 39.5} \qquad [16.18.20]$$

Typical conditions of $M_a \approx 29.0$, $M_p \approx 28$, $T_a \approx 288\,\mathrm{K}$ and $T_1 = 2250\,\mathrm{K}$ yield $\beta \approx 2.85$.

For a tilted jet, in which the hole axis is in the wind direction and at an angle θ_j to the horizontal, it has been shown by laboratory experiments that the flame length reduces as the jet is tilted into the wind, i.e. as θ_j increases, because the air entrainment coefficient increases. A linear relation holds between L_B/D_s and θ_j. Then for the actual length L_B of the flame

$$\frac{L_B}{D_s} = 163 - 0.64\theta_j \qquad [16.18.21a]$$

or

$$L_B = 105.4D_s[1 - 6.07 \times 10^{-3}(\theta_j - 90)] \qquad [16.18.21b]$$

On the assumption that L_B scales similarly with θ_j for all wind speeds and directions, the general correlation for L_B is

$$L_B = L_{Bo}[0.51\exp(-0.4v) + 0.49][1 - 6.07 \times 10^{-3}(\theta_{jv} - 90)] \quad [16.18.22]$$

where θ_j is the angle between the hole axis and the horizontal (°) and θ_{jv} is the angle between the hole axis and the wind vector in the plane containing the hole axis, the flame axis and the wind vector (°).

For the angle α between the axis of the orifice and that of the flame

$$\alpha = \frac{1}{\xi(L_{Bo})}\{8000R + \xi(L_{Bo})(\theta_{jv} - 90)[1 - \exp(-25.6R)]\} \quad R \le 0.05 \quad [16.18.23a]$$

$$\alpha = \frac{1}{\xi(L_{Bo})}\{1726(R - 0.026)^{\frac{1}{2}} + 134 + \xi(L_{Bo})(\theta_{jv} - 90) \times [1 - \exp(-25.6R)]\} \quad R > 0.05 \quad [16.18.23b]$$

where α is the angle between the hole axis and the flame axis (°).

For the lift-off distance b of the frustrum of the flame, by geometry

$$b = L_B \frac{\sin(\alpha - \alpha_b)}{\sin\alpha} \quad [16.18.24a]$$

or

$$b = L_B \frac{\sin K\alpha}{\sin\alpha} \quad [16.18.24b]$$

with

$$K = \frac{\alpha - \alpha_b}{\alpha} \quad [16.18.25]$$

where b is the lift-off height (m) and α_b is the angle between the hole axis and the line joining the top of the flame to the centre of the hole (°).

K was correlated as follows:

$$K = 0.185\exp(-20R) + 0.015 \quad 0.005 \le R \le 3 \quad [16.18.26]$$

For $\alpha = 0^o$ or 180°

$$b = KL_B \quad [16.18.27]$$

For the length R_L of the frustrum, by geometry

$$R_L = (L_B^2 - b^2\sin^2\alpha)^{\frac{1}{2}} - b\cos\alpha \quad [16.18.28]$$

For the width W_1 of the base of the frustrum the following correlation was obtained:

$$W_1 = D_s[13.5\exp(-6R) + 1.5] \times \left\{1 - \left[1 - \frac{1}{15}\left(\frac{\rho_a}{\rho_j}\right)^{\frac{1}{2}}\right]\exp(-70\xi(D_s)CR)\right\} \quad [16.18.29]$$

with

$$C = 1000\exp(-100R) + 0.8 \quad [16.18.30]$$

$$\xi(D_s) = \left(\frac{g}{D_s^2 u_j^2}\right)^{\frac{1}{3}} D_s \quad [16.18.31]$$

where W_1 is the width of the frustrum base (m).

For the width of the top of the frustrum W_2, the correlation obtained was

$$W_2 = L_B[0.18\exp(-1.5R) + 0.31][1 - 0.47\exp(-25R)] \quad [16.18.32]$$

where W_2 is the width of the frustrum top (m).

For the surface area A of the flame, including the two end discs, by geometry

$$A = \frac{\pi}{4}(W_1^2 + W_2^2) + \frac{\pi}{2}(W_1 + W_2)\left[R_L^2 + \left(\frac{W_2 - W_1}{2}\right)^2\right]^{\frac{1}{2}} \quad [16.18.33]$$

where A is the surface area of the flame (m^2).

The surface emissive power of the flame is then

$$E = \frac{F_r Q}{A} \quad [16.18.34]$$

where F_r is the fraction of heat radiated, E is the surface emissive power (kW/m^2) and Q is the net heat release rate (kW).

The fraction F_r of heat radiated was found to correlate with gas velocity u_j as follows:

$$F_r = 0.21\exp(-0.00323u_j) + 0.11 \quad [16.18.35]$$

The radiation incident on a target is then

$$I = \tau FE \quad [16.18.36]$$

where F is the view factor, I is the radiation incident on the target (kW/m^2) and τ is the atmospheric transmissivity.

A version of the Chamberlain model incorporated in the computer code SAFETI has been described by J. Cook, Bahrami and Whitehouse (1990).

16.18.7 Johnson, Brightwell and Carsley model

A.D. Johnson, Brightwell and Carsley (1994) have described a model for a jet flame of natural gas issuing horizontally, which is an extension of the flare model of Chamberlain (1987), already described. The model was developed in conjunction with large-scale tests on natural gas flames.

As in the original model, the flame is represented as the frustrum of a cone with the maximum width at the end furthest from the origin. For the flame shape the treatment is as follows. The momentum flux of the expanded jet is

$$G = \frac{\pi\rho_j u_j^2 d_j^2}{4} \quad [16.18.37]$$

where d_j is the diameter of the expanded jet (m), G is the initial momentum flux of the expanded jet (N), u_j is the velocity of the expanded jet (m/s) and ρ_j is the density of the expanded jet (kg/m^3). The parameters d_j, u_j and ρ_j are as defined by Chamberlain.

A Richardson number $\xi(L)$ is defined as

$$\xi(L) = \left(\frac{\pi\rho_a g}{4G}\right)^{\frac{1}{5}} L \qquad [16.18.38]$$

where g is the acceleration due to gravity (m/s^2), L is a characteristic length (m) and ρ_a is the density of air (kg/m^3).

The length scale L is the length over which the buoyancy force acts and is taken as the flame length L_{bo} for a vertical flame in still air. The value of L_{bo} is given by a correlation derived by Khalhatgi (1984). L_{bo} is obtained as the solution of the equations

$$\Psi = 0.2 + 0.024\xi(L_{bo}) \qquad [16.18.39]$$

with

$$\Psi = \left(\frac{2.85 D_s}{L_{bo} W}\right)^{\frac{2}{3}} \qquad [16.18.40]$$

where D_s is the effective source diameter (m), L_{bo} is the flame length in still air (m), W is the mass fraction of the fuel in a stoichiometric mixture with air and Ψ is a parameter. The effective source diameter is the throat diameter of an imaginary nozzle from which air at ambient density issues with the same mass flow and momentum as the fuel:

$$D_s = d_j\left(\frac{\rho_j}{\rho_a}\right)^{\frac{1}{2}} \qquad [16.18.41]$$

The authors indicate that range of validity of the relation for L_{bo} is $2 < \xi(L_{bo}) < 20$.

The flame shape is defined relative to the x, y and z co-ordinates, where x, y and z are the distances in the release direction, the vertical direction and the crosswind direction, respectively. The position of the flame is determined by the relative effects of the initial jet momentum flux and the wind momentum fluxes in the x, or release, direction and in the z direction, perpendicular to the flame. The balance of these momentum fluxes is characterized by the two parameters

$$\Omega_x = \left(\frac{\pi\rho_a}{4G}\right)^{\frac{1}{2}} L_{bo} u_a \qquad [16.18.42]$$

$$\Omega_z = \left(\frac{\pi\rho_a}{4G}\right)^{\frac{1}{2}} L_{bo} w_a \qquad [16.18.43]$$

where u_a is the wind speed in the release direction (m/s), w_a is the wind speed perpendicular to the release (m/s) and Ω_x and Ω_z are parameters.

The end of the flame frustrum is correlated by a term defining the end of the flame in still air multiplied by a term allowing for the effect of the wind. It was found experimentally that a cross-wind had little effect on the position of the flame in the x direction so that the influence of the parameter Ω_z could be neglected. Then for the x position of the flame X

$$\frac{X}{L_{bo}} = f(\xi)[1 + r(\xi)\Omega_x] \qquad [16.18.44]$$

with

$$f(\xi) = 0.55 + (1 - 0.55)\exp(-0.168\xi) \qquad \xi \le 5.11 \qquad [16.18.45a]$$

$$f(\xi) = 0.55 + (1 - 0.55)\exp[-0.168\xi - 0.3(\xi - 5.11)^2] \qquad \xi > 5.11 \qquad [16.18.45b]$$

$$r(\xi) = 0 \qquad \xi \le 3 \qquad [16.18.46a]$$

$$r(\xi) = 0.82\{1 - \exp[-0.5(\xi - 3.3)]\} \qquad \xi > 3 \qquad [16.18.46b]$$

where f and r are parameters. A limit is placed on the x position by setting a maximum value of X/L_{bo} of 1.0. Similarly, for the y position of the flame Y

$$\frac{Y}{L_{bo}} = h(\xi)[1 - c(\xi)\Omega_x] \qquad [16.18.47]$$

with

$$h(\xi) = (1 + 1/\xi)^{-8.78} \qquad [16.18.48]$$

$$c(\xi) = 0.02\xi \qquad [16.18.49]$$

The y position is confined within the range $0 \le Y/L_{bo} \le 1.0$.

The maximum diameter of the flame, at the point furthest from the origin, is given by the correlation

$$\frac{W_2}{Lb_{xy}} = -0.004 + 0.0396\xi - \Omega_x(0.0094 + 9.5 \times 10^{-7}\xi^5) \qquad [16.18.50]$$

with

$$Lb_{xy} = (X^2 + Y^2)^{\frac{1}{2}} \qquad [16.18.51]$$

where W_2 is the maximum diameter of the flame (m) and Lb_{xy} is a parameter (m). For a realistic flame shape, W_2 must be greater than W_1 and less than Lb_{xy}.

The lift-off distance of the flame is

$$b = 0.141(G\rho_a)^{\frac{1}{2}} \qquad [16.18.52]$$

where b is the lift-off distance (m). The minimum diameter of the flame is

$$\frac{W_1}{b} = -0.18 + 0.081\xi \qquad [16.18.53]$$

where W_1 is the minimum diameter of the flame (m). The flame cannot become narrower than the forced convection limit and W_1/b has a minimum value of 0.12.

The z position of the flame is given by the correlation

$$\frac{Z}{X - b} = 0.178\Omega_z \qquad [16.18.54]$$

This completes the model for the flame shape. For the thermal radiation, the surface emissive power is given by

$$S = S_\infty[1 - \exp(-kL)] \qquad [16.18.55]$$

with

$$S_\infty = \frac{F_{s\infty} Q}{A} \qquad [16.18.56]$$

where A is the total surface area of the flame (m^2), $F_{s\infty}$ is the fraction of heat radiated for flames which emit black body radiation, k is a gray gas absorption coefficient (m^{-1}), L is a length representing the emitting path length (m), Q is the net heat release rate (kW), S is the surface emissive power (kW/m^2) and S_∞ is the black body surface emissive power (kW/m^2). The value of k

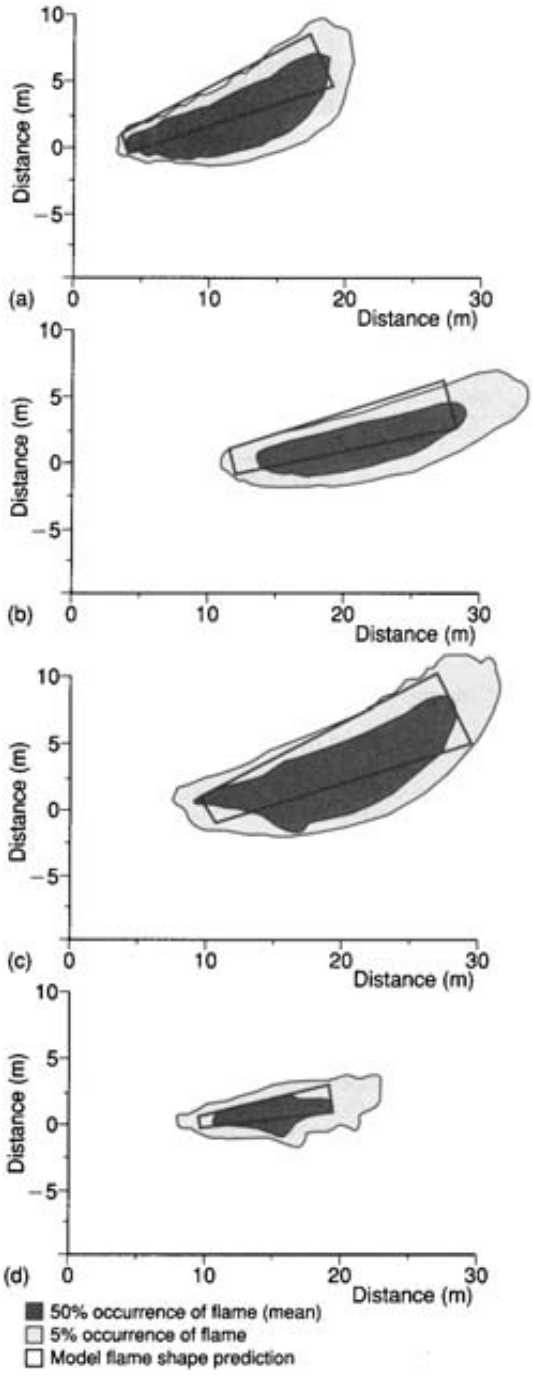


Figure 16.104 *Flare flames: flame dimensions for the model of Johnson, Brightwell and Carlsey. Comparison between model predictions and experimental results (A.D. Johnson, Brightwell and Carlsey, 1994): (a) Test 1040, Type B; (b) Test 1033, Type D; (c) Test 1083 Type C; and (d) Test 1089, Type E*

was found to be $0.4\,m^{-1}$, whilst $F_{s\infty}$ was correlated as follows:

$$F_{s\infty} = 0.21 \exp(-0.00323 u_j) + 0.14 \quad [16.18.57]$$

The thermal radiation on the target is then

$$q = (F_{sd}S_{sd} + F_{en}S_{en})\tau \quad [16.18.58]$$

where F is the view factor, q is the thermal radiation incident on the target (kW/m^2) and τ is the atmospheric transmissivity. Subscripts en and sd denote the end and the side of the flame, respectively.

Figure 16.104 shows a set of comparisons between the results obtained with the model and those obtained from the experimental tests for four standard trial conditions B–E.

16.18.8 Cook *et al.* model

A model for a flare of natural gas has been given by D.K. Cook, Fairweather, Hammonds and Hughes (1987). This model also is relatively complex.

16.19 Jet Flames

There is a wide variety of situations in which a jet flame, or ejected flame, can occur in the process industries, either by design or by accident. The principal situations in which flames occur by design are in burners and flares. Flames on burners are not treated here. Those on flares have been considered in Section 16.18. Ejection of flammable fluid from a vessel, pipe or pipe flange can give rise to a jet flame if the material ignites. An intermediate situation, and one which particularly concerns the designer, is where the jet flame results from ignition of flammable material vented from a pressure relief valve.

Scenarios involving jet flames are not easy to handle, since a large jet flame may have a substantial 'reach', sometimes up to 50 m or more.

Jet flames have been involved in a number of accidents. Perhaps the most dramatic were the large jet flames from the gas riser on the Piper Alpha oil platform, as described in Appendix 19. In other cases jet flames from pressure relief valves have caused adjacent vessels to overheat and burst, giving a boiling liquid expanding vapour explosion, or BLEVE. Such was the case at Mexico City, as described in Appendix 4.

16.19.1 Experimental studies

Much of the early experimental work relevant to jet flames was concerned with flares. An account of this work was given in Section 16.18. There is now, however, a growing interest in the jet flame in its own right.

Table 16.69 lists some studies on flares and on jet flames. Investigations of the combustion of large scale jet releases of liquefied flammable gas have been undertaken by Shell, BP and British Gas, both separately and in co-operation.

The work done covers a variety of jet flames, including flames of natural gas and of LPG. Representative accounts of work using natural gas are those by Chamberlain (1987) and A.D. Johnson, Brightwell and Carsley (1994) at Shell, and by D.K. Cook, Fairweather, Hammonds and Hughes (1987) at British Gas.

Accounts of work on jet flames of LPG at Shell and British Gas have been given by Hirst (1984) and Tam

Table 16.69 *Some studies on flares and on jet flames*

A Studies of flares	
Experimental studies of heat radiation	Studies referenced in API RP 521:1990
Experimental and theoretical studies of flare dimensions and heat radiation	Brzustowksi and Sommer (1973)
Experimental and theoretical studies of flare characteristics	de Faveri *et al.* (1985)
Theoretical model of flare dimensions and heat radiation	Chamberlain (1987)
Experimental and theoretical studies of flare dimensions and heat radiation	D.K. Cook, Fairweather, Hammonds and Hughes (1987); D.K. Cook, Fairweather, Hankinson and O'Brien (1987); D.K. Cook (1991a,b)
Experimental and theoretical studies of flare dimensions and heat radiation	A.D. Johnson, Brightwell and Carsley (1994)
B Studies of jet flames	
Theoretical model of jet flame dimensions	Burke and Schumann (1928a,b)
Theoretical model of jet flame dimensions	Hawthorne, Weddell and Hottell (1949)
Theoretical model of jet flame dimensions and heat radiation	Craven (1972, 1976)
Experimental studies of jet flames of LPG	Hirst (1984)
Experimental and theoretical studies of jet flame dimensions and heat radiation	Sonju and Hustad (1984); Hustad and Sonju (1986)
Experimental and theoretical study of jet flames on rail tank cars	Tunc and Venart (1984/85b)
Empirical model of jet flame dimensions and hazard range	Considine and Grint (1985)
Empirical model of jet flame dimensions and heat radiation	Clay *et al.* (1988); Grint (1989)
Experimental studies of jet flames of LPG	Tam and Cowley (1989)
Theoretical model of gas pipeline jet flame heat radiation	D.A. Carter (1991)

and Cowley (1989). The work on flames formed part of a study of emission and gas dispersion of jets as well as of combustion.

Hirst (1984) describes experiments using liquefied propane. Tests were carried out using orifices ranging from 9 to 52 mm in diameter and pressures from about 6 to 20 bar. Both vertical and horizontal releases were studied.

A series of tests were done with vertical releases. The liquid rose in a strongly divergent cone bending with the wind. The cone angle was typically 30° for the plume but up to 90° in the flash region. The releases usually reached a steady state before ignition. The visible clouds at ignition were large, extending up to 45 m vertically and 70 m downwind. In most cases a fireball formed and in several tests rose to 100 m; the most fully developed fireballs occurred at low wind speeds. Plate 14 shows the formation of a fireball in one of the vertical releases.

The overpressures generated by the flames were also measured. The maximum observed overpressures fell from some 3 mbar at 20 m from the release point to about 0.8 mbar at 100 m.

Other tests were done with horizontal releases. One of features measured in these trials was the distance reached by the flame. Figure 16.105 gives for a 50 mm diameter pipe the relation between the mass flow and the impingement distance of the flame.

One of the trials is illustrated in Plate 12, which shows a 35 m long jet flame from a full bore release of 7.9 kg/s from a 50 mm pipe at a pressure of 13 barg. The combustion energy was 365 MW. The maximum surface emissive power was 250 kW/m^2 and occurred 25 m from the release point and just before the flame underwent transition from the momentum-dominated to the buoyancy-dominated condition.

However, for such full bore discharges the heat radiation within the flame was complex and steady heat fluxes were mainly in the range 50–220 kW/m^2 and depended on the discharge conditions and the target distance. The maximum temperature occurred at a distance of 4 m and had a value of 1570 K.

The problem of heat radiation from a flame on a pressure relief valve on a rail tank car onto the surface of the latter has been studied by Tunc and Venart (1984/85b). Experiments were conducted on ignited releases from pressure relief valves on tank cars.

16.19.2 Empirical features

A jet flame resulting from the ignition of a leak of flammable fluid at the leak aperture is a diffusion flame. The basic characteristics of such a flame have been outlined in Section 16.12.

At low velocities the flame is generally attached to the point of release, but at higher velocities it becomes

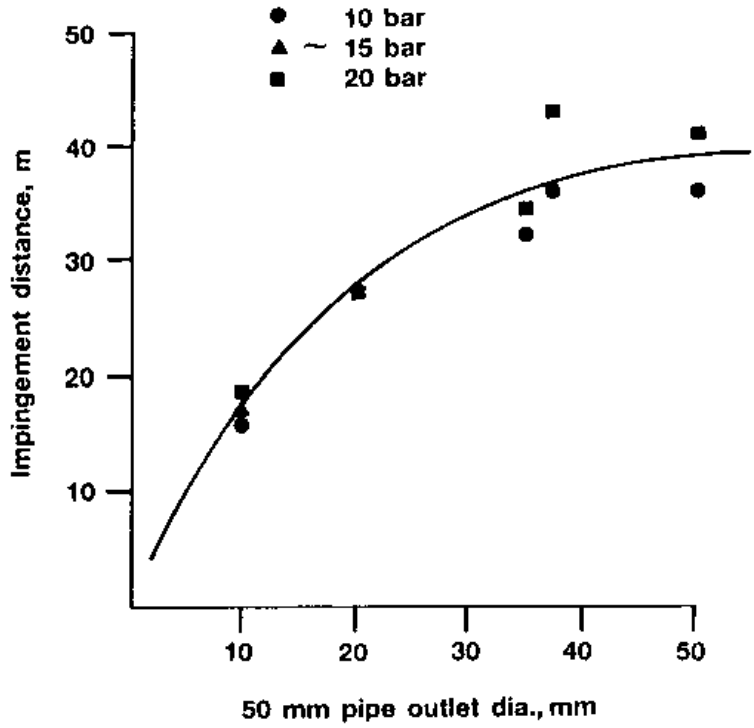


Figure 16.105 *Jet flames: flame impingement distance vs mass flow for propane (Tam and Cowley, 1989) (Courtesy of Gastech)*

detached, the distance between the orifice and the flame increasing with velocity so that it may become unstable and lift off, thus being extinguished. If, however, the flame impinges on an obstruction, this may serve to stabilize it.

As already stated, jet flames can have a considerable reach. The flame impingement distance can be up to 50 m or more. The reach is sometimes expressed in terms of the ratio of the flame length to the orifice diameter, and values of this l/d ratio in excess of 300 are quoted.

Generally, the length of a jet flame over the range of practical interest is approximately proportional to the square root of the mass flow. This is the implication of the API correlation for the flame length on a flare and of the work on propane jet flames just described. It is also implied in a number of models.

The graph given in Figure 16.105 is fitted approximately by the relation

$$l_i \approx 6m^{0.5} \qquad 0 < m < 50 \qquad [16.19.1]$$

where l_i is the impingement distance (m) and m is the mass flow (kg/s).

The fraction of heat radiated by a jet flame is a function of the fuel, being less for hydrogen and methane than for propane. It tends to increase and reach a maximum as the orifice diameter increases. It usually lies in the range 0.15–0.3.

For diffusion flames in general the flame temperatures have been discussed by Gugan (1976). He quotes values of some 1600°C for laminar diffusion flames and 2000°C for turbulent diffusion flames, the heat release in the latter being an order of magnitude greater. The maximum flame temperature in a gas jet flame is of the order of 2000°C.

The maximum flame temperatures observed in the work on jet flames of liquefied propane were of the order of 1300°C. Further, in this work on liquefied propane the values of the surface emissive power up to 250 kW/m^2 were observed, but these are spot values and do not occur over the whole flame.

16.19.3 Modelling of jet flames

By comparison with fireballs and pool fires, with jet flames the number of possible scenarios to be considered is much greater. The case mainly treated is that of a vertical flame on an upward pointing jet, in calm conditions or in wind. Another case occurs where the jet points upwards not vertically but at an angle. In this case there may be a variety of wind directions, confluent with, opposed to or across the jet. A third case is the horizontal jet, for which again the wind direction may be confluent, opposed or across.

Different workers have assumed different geometries for the jet. These include a cone (e.g. Craven, 1972), a cylinder (e.g. Croce and Mudan, 1986) and a frustrum (e.g. Chamberlain, 1987). One consequence of this is that there is no generally applicable view factor and that the view factor to be used has to be developed for the particular geometry, except in so far as the point source method is applicable.

A model of a jet flame was formulated by Burke and Schumann (1928a,b) and was later taken up by Savage (1962). Another early model is that of Hawthorne, Weddell and Hottel (1949). Work on the modelling of jet flames has been done by Craven (1972), Bilger (1975, 1976, 1977, 1979, 1989), MITI (1976), H.A. Becker and Liang (1978, 1982), R. Becker (1980a,b), Kalghati (1981–, 1983, 1984), de Faveri, Fumarola and co-workers (Fumarola *et al.*, 1983; de Faveri *et al.*, 1985), Peters and co-workers (Peters and Williams, 1983; Peters and Göttgens, 1991), Hustad and Sonju (Sonju and Hustad, 1984; Hustad and Sonju, 1986), Croce and Mudan (1986) and Duijm (1994).

Work at Shell includes that by Chamberlain (1987) and A.D. Johnson, Brightwell and Carsley (1994).

Birch and co-workers at British Gas have conducted a series of studies on unignited and ignited jets (Birch *et al.*, 1978, 1984, 1988, 1989). Also at British Gas, D.K. Cook, Fairweather and co-workers have modelled natural gas flares (D.K. Cook, Fairweather, Hammonds and Hughes, 1987; D.K. Cook, Fairweather, Hankinson and O'Brien, 1987; D.K. Cook, 1991a,b; Fairweather *et al.*, 1991; Fairweather, Jones and Linstedt, 1992)

Models used by the HSE have been described by Clay *et al.* (1988), Grint (1989) and D.A. Carter (1991).

The set of models of fire events given by Considine and Grint (1985) includes one for a jet flame.

Many jet flame models derive from work on the modelling of flares, and most models are for jet flames of gas, particularly natural gas. There are also a few models for jet flames of a flashing liquid such as LPG.

Models for jet flames of LPG include those given by Clay *et al.* (1988), Grint (1989) and J. Cook, Bahrami and Whitehouse (1990).

Some of the principal jet flame models are now described.

16.19.4 Hawthorne, Weddell and Hottel model

One of the first models of a jet flame was that given by Hawthorne, Weddell and Hottel (1949). They envisage the flame as an inverted cone with the apex on the orifice. The equations for the length of the flame and for the diameter at the top of the cone have been given above as Equations 16.3.3 and 16.3.4, respectively.

16.19.5 Bzrustowski and Sommer model

The model of Brzustowksi and Sommer (1973), which is given in API RP 521 as an alternative to the simplified API method for flare design and has been described in Section 16.18, is also used as a model for a jet flame.

16.19.6 Craven model

A model of a jet flame developed for the purpose of designing of emergency relief vents has been described by Craven (1972). He gives the following method of estimating the heat flux incident on a target near the flame.

The flame model considered is shown in Figure 16.106. The dimensions of the flame are estimated using the correlation of Hawthorne, Weddell and Hottel given in Equations 16.3.3 and 16.3.4. The flame temperature is assumed to be 2300 K, a value which is equal to or somewhat greater than the adiabatic flame temperature for most hydrocarbons. The emissivity of the flame is taken as unity. The radiant heat flux E is then

$$E = \epsilon\sigma T^4 \qquad [16.19.2]$$

where E is the radiant heat flux (W/cm^2), T is the absolute temperature of the flame (K), ϵ is the emissivity of the flame, and σ is the Stefan–Boltzmann constant. The emissivity is assumed to be unity, so that for a flame temperature of 2300 K

$$E = 160\ \mathrm{W/cm^2} = 1600\ \mathrm{KW/m^2}$$

The heat flux and view factors for targets at points X, Y and Z in Figure 16.106 are considered. At point X, which is directly beneath the vent, the emissivity may be taken as unity. For a horizontal target at this point the flame is viewed as a disc and the view factor F_X (Howell, 1982-configuration B-11) is

$$F_X = \frac{r^2}{(l+h)^2 + r^2} \qquad [16.19.3]$$

where h is the height of the vent orifice (m), l is the length of the flame (m), and r is the radius of the flame at its tip (m).

For radiation at point Z the flame is treated as a rectangular radiator ABCD with an emissivity of unity. For a horizontal target at this point the configuration factor F_Z is

$$F_Z = \frac{xr}{\pi}\left[\frac{1}{(h_1^2 + x^2)} - \frac{1}{(h_2^2 + x^2)}\right] \qquad [16.19.4]$$

with

$$h_1 = h + l/2 \qquad [16.19.5a]$$

$$h_2 = h + l \qquad [16.19.5b]$$

where h_1 is the distance from the ground to the bottom of the radiator ABCD (m), h_2 is the distance from the ground to the top of the radiator (m) and x is the distance between points X and Z (m). The value of the view factor F_Z passes through a maximum as x increases.

The radiation at point Y is more difficult to determine, but an estimate may be made as follows. At this point part of the radiation comes from the thin part of the flame. In this case the area of the radiator ABEJ is approximated by $\frac{3}{4}rl$ and the view factor F_Y is given very approximately by the expression

$$F_Y \approx \frac{rl}{\pi y^2} \qquad [16.19.6]$$

with

$$y \approx 10 D_{max} \qquad [16.19.7]$$

where D_{max} is the maximum cone diameter (m) and y is the horizontal distance to the axis of the flame (m).

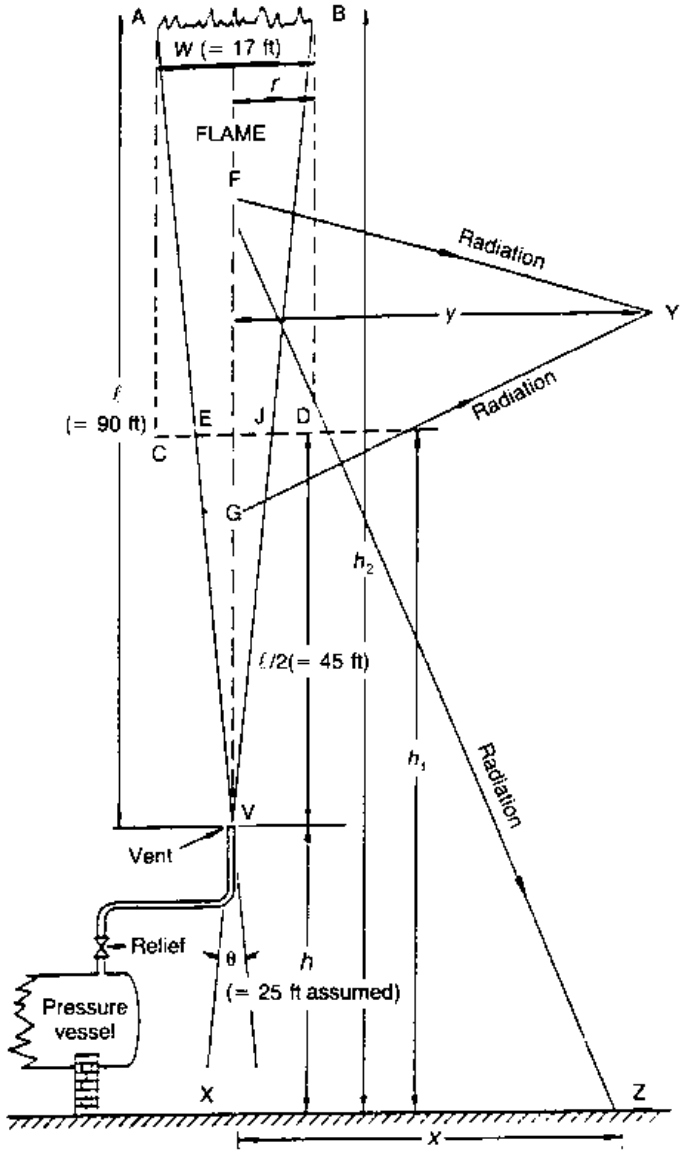


Figure 16.106 *Jet flames: flame dimensions for the Craven model (after Craven, 1972) (Courtesy of the Institution of Chemical Engineers)*

Craven points out that, whilst the above treatment applies to the highly turbulent flame occurring during the main discharge, a different situation occurs as this discharge subsides. In this stage there may exist for a short period a flame which is much less turbulent. Such a flame will tend to be larger but its temperature will be much less and the net effect is that the heat radiated is also less.

He also draws attention to the strong forces which can be exerted by a jet reaction when material under pressure is vented, and to the possibility that if the vent supports are inadequate, the vent pipe, and hence the flame, may be deflected from the vertical.

The method described is not intended to be used for flames on flare stacks, which are not highly turbulent and are therefore cooler.

Craven (1976) has compared estimates made by his method with observations given by R.O. Parker (1974) based on the ignition of an accidental discharge of natural gas. The results of the comparison of predicted and observed thermal radiation fluxes to targets side-on to the turbulent flame brush are given in Table 16.70.

Table 16.70 *Thermal radiation from a flame on a vent: comparison of predicted and observed radiation fluxes to side-on targets (Craven, 1976) (Courtesy of the Institution of Chemical Engineers)*

Distance ratio[a]	*Heat radiation flux* (W/cm^2)	
	Predicted[b]	*Observed*[c]
3.3	9.0	7.0
6.67	2.3	2.8
10	1.0	1.37
13.3	0.6	0.8
16.7	0.4	0.51

[a] Ratio of the distance from the flame to the target to the flame diameter.
[b] Predicted using the method of Craven (1972), as described in the text.
[c] Observed data given by R.O. Parker (1974).

The method given by Craven is essentially intended for design rather than for hazard assessment. In particular, the value assumed for the flame temperature is at the upper end of the range that is likely to occur in practice.

16.19.7 Hustad and Sonju model

Another jet flame model is that of Hustad and Sonju (Sonju and Hustad, 1984; Hustad and Sonju, 1986). Following earlier work by Suris, Flankin and Shoring (1977), Hustad and Sonju correlate the flame dimension in terms of the Froude number Fr. Their equations are

$$\frac{H}{d} = A\,\mathrm{Fr}^m \qquad [16.19.8]$$

$$\frac{D}{d} = B\,\mathrm{Fr}^m \qquad [16.19.9]$$

with

$$\mathrm{Fr} = \frac{u^2}{gd} \qquad [16.19.10]$$

where d is the diameter of the orifice (m), D is the diameter of the flame (m), g is the acceleration due to gravity (m/s^2), H is the height of the flame (m), u is the gas velocity at the nozzle exit (m/s), A and B are constants and m is an index.

For vertical flames they obtained values of A of 21 for methane and 27 for propane, and values of B of 2.5 for methane and 4 for propane. For both gases the value of m in both equations was 0.2 for $\mathrm{Fr} \leq 10^5$, but zero for $\mathrm{Fr} > 10^5$. Thus for both gases the value of the ratio H/D was constant, being 8.4 for methane and 6.75 for propane.

For horizontal flames of propane Equations 16.19.8 and 16.19.9 again applied. For Equation 16.19.8 the values of the constant just given were again applicable, but for Equation 16.19.9 the values of B and m were 10 and 0.156, respectively.

The height H^* over which the flame radiates heat is given as

$$H^* = H - h \qquad [16.19.11]$$

with

$$\frac{h}{d} = C\left(\frac{d}{u}\right)^{-1} \qquad [16.19.12]$$

where h is the lift-off height (m), H^* is the flame radiation height (m) and C is a constant. The value of the constant C is $3.6 \times 10^{-3}\ s^{-1}$.

For the fraction of heat radiated, Hustad and Sonju give

$$F = 4.74Q^{-0.2} + 11.6Q^{0.4} \qquad 1 < Q < 7 \qquad [16.19.13]$$

where F is the fraction of heat radiated and Q is the heat release rate (MW).

Thus, for example, for propane at heat release rates of 1 and 7 MW the fractions of heat radiated are 0.163 and 0.285, respectively.

16.19.8 Chamberlain model and Johnson, Brightwell and Carsley model

The flare models of Chamberlain (1987) and A.D. Johnson, Brightwell and Carlsey, described in Section 16.18, also have application as models for a jet flame in an accident. The latter model is for a horizontal flame, which is the orientation of most interest in that context.

16.19.9 Cook, Bahrami and Whitehouse model

J. Cook, Bahrami and Whitehouse (1990) have described the jet flame models incorporated in the computer code SAFETI. There are two such models.

The first model is described as based on the API RP 521 jet flame model. The relations given are

$$L = 0.00326[\dot{m}(-\Delta H_c)]^{0.478} \qquad [16.19.14]$$

$$R_s = 0.29s[\log_{10}(L/s)]^{0.5} \qquad [16.19.15]$$

where $(-\Delta H_c)$ is the heat of combustion (J/kg), L is the length of the flame (m), $\dot{m}$ is the mass flow (kg/s), R_s is the radius of the flame at distance s (m) along the centre line (m).

It is assumed that the jet is emitted either vertically upwards or horizontally downwind. For a vertical jet which may be bent over by the wind, the trajectory is constructed using the API prescription according to the equation

$$\frac{dz}{dx} = \frac{1.6\pi D_j u_j}{u_w}\left(\frac{1}{s} - \frac{1}{L}\right) \qquad [16.19.16]$$

where D_j is the diameter of the jet (m), u_j is the velocity of the jet (m/s), u_w is the wind velocity (m/s) and x and z are the distances in the horizontal and vertical directions (m). Then the trajectory of the centre line of the jet flame is

$$x(s) = \int_0^s \frac{ds'}{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{0.5}} \qquad [16.19.17]$$

$$z(s) = \int_0^s \frac{ds'}{\left[1 + \left(\frac{dx}{dz}\right)^2\right]^{0.5}} \qquad [16.19.18]$$

The other jet flame model used is the Chamberlain model.

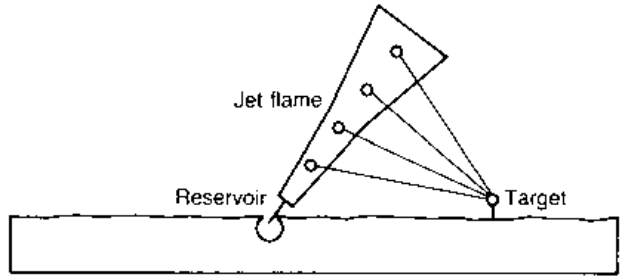


Figure 16.107 *Jet flames: flame dimensions for the Carter model of gas pipeline release (D.A. Carter, 1991) (Courtesy of Butterworth-Heinemann)*

16.19.10 Carter model

A model for the thermal radiation incident on a target from a jet flame on a gas pipeline has been given by D.A. Carter (1991). The flame assumed is as shown in Figure 16.107. Its dimensions are based on its state 30 seconds after release. Carter states that the model of the flame itself is based on that of Chamberlain, but otherwise gives no details.

The flame is treated as a multiple source radiator. For each source in the flame the relation for the thermal radiation is

$$q = \frac{F_r(-\Delta H_c)\dot{m}\tau}{4\pi x^2} \qquad [16.19.19]$$

with

$$\tau = 1 - 0.0565 \ln x \qquad [16.19.20]$$

where F_r is the fraction of heat radiated, $(-\Delta H_c)$ is the heat of combustion (kJ/kg), $\dot{m}$ is the mass flow (kg/s), q is the heat incident on the target (kW/m^2), x is the distance from the source to the target (m) and τ is the atmospheric transmissivity.

The flame model is embodied in the computer code SHELF and the heat radiation model in the code MAJESTIC.

As an illustration of the model, consider the example given by Carter. The problem is the determination of the heat radiation contours for a release of ethylene from a 9 in. pipeline at 100 bar with a mass flow of 43.7 kg/s. The flame length is 39 m and the flame tilt from vertical 11.5°. The heat of combustion is 4.771×10^4 kJ/kg and the fraction of heat radiated is 0.1284. Then from Equation 16.19.19 the contours of incident heat are as shown in Figure 16.108.

16.19.11 MITI model

Turning now to models for jet flames of flashing liquids, an equation for the length of a diffusion flame on the surface of an oil storage tank as a function of the Froude number has been given by Werthenbach (1971a,b, 1973). This equation has been adapted by the MITI (1976) for the jet flame formed if liquefied flammable gas blows a bursting disc and then ignites:

$$q = 0.000\,678\,5\,L^{2.5} \qquad [16.19.21]$$

where L is the flame length (m) and q is the fuel flow (kg/s). The use of this equation to correlate the length of ejected flames from fire engulfed vessels is discussed below.

16.19.12 Considine and Grint model

Considine and Grint (1985) have derived a model for a jet flame based on the work of the MITI (1976) on liquid ethylene. The flame is assumed to be conical. The model equations are

$$L = 9.1\,\dot{m}^{0.5} \qquad [16.19.22]$$

$$W = 0.25L \qquad [16.19.23]$$

where L is the length of the flame (m), $\dot{m}$ is the mass flow (kg/s), and W is the half-width of the flame tip (m).

This model also includes relations for the hazard range of the flame. These are given in Section 16.39.

16.19.13 Clay *et al.* model

Clay *et al.* (1988) describe a set of models used by the HSE for hazard assessment, one of which is for a jet flame of LPG.

The flame length is given as

$$F = \frac{(H_c m)^{0.444}}{161.66} \qquad [16.19.24]$$

where F is the flame length (m), H_c is the heat of combustion (J/kg) and m is the mass flow (kg/s).

The flame is modelled as a point source radiator with heat radiated from a point located 4/5 of the flame length from the origin. For the thermal radiation the relation used is

$$q = \frac{fH_c m\tau \times 10^{-3}}{4\pi x^2} \qquad [16.19.25]$$

with

$$\tau = 1 - 0.0565 \ln x \qquad [16.19.26]$$

where f is the fraction of heat radiated, q is the thermal radiation received by the target (kW/m^2), x is the distance between the source and the target (m) and τ is the atmospheric transmissivity.

Graphs for the flame length and thermal radiation from a jet flame of LPG are given by Grint (1989) and appear to give results similar to those obtained with this model.

16.19.14 Modified Cook, Bahrami and Whitehouse model

J. Cook, Bahrami and Whitehouse (1990) state that for jet flames from a liquid or from a two-phase liquid–vapour mixture Chamberlain's model can be adapted by

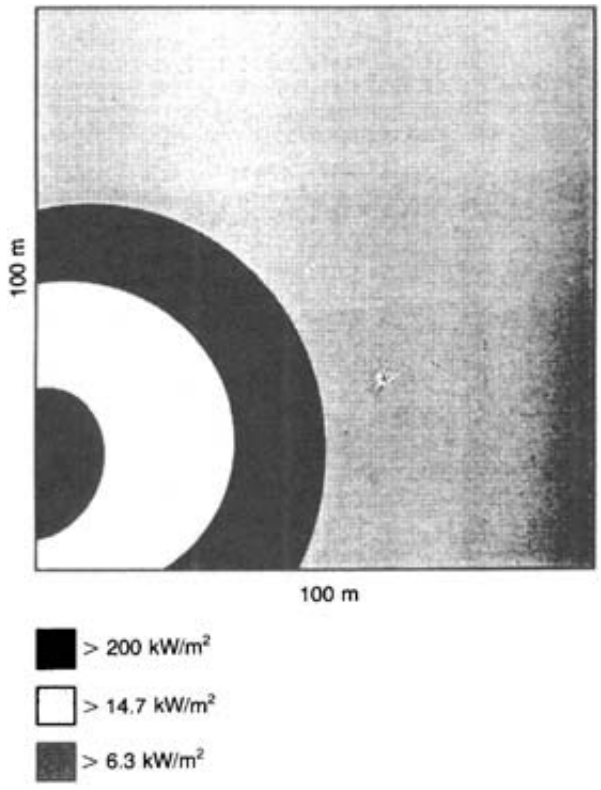


Figure 16.108 *Jet flames: heat radiation contours for illustrative example of flame from gas pipeline release (D.A. Carter, 1991). A > 200 kW/m²; B > 14.7 kW/m² and C > 6.3 kW/m² (Courtesy of Butterworth-Heinemann)*

the following modification of the effective source diameter:

$$D_s = D_j \frac{(\rho_j \rho_v)^{\frac{1}{2}}}{\rho_a} \qquad [16.19.27]$$

and the lift-off distance b modified as follows:

$$b = 0.015L \qquad [16.19.28]$$

where ρ_v is the density of the vapour (kg/m^3).

16.19.15 Tunc and Venart model

The problem of heat radiation from a flame on a pressure relief valve on a rail tank car onto the surface of the latter has been studied by Tunc and Venart (1984/85b). Vertical and tilted flames are considered. The flame is modelled as a radiating surface rather than a point source. The view factor for a tilted flame is given.

16.19.16 View factors

In some applications it is sufficient to treat the jet flame as a point source radiator. In other cases it may be necessary to use a more accurate view factor. For a view factor based on the point source method use may be made of Equations 16.13.101–16.13.103.

View factors for some of the jet flame models just described have been given by Crocker and Napier (1988a). For the model by Hawthorne, Weddel and Hottel (1949) of a vertical flame, Crocker and Napier refer to the work of Tunc and Venart (1984/85b), who treat the flame as conical, and quote for the view factor F in this case the following integral equations given by Becker (1980a):

$$F = \frac{2}{\pi} \int_h^{h+L} \frac{[x \sin \psi + (z \tan \alpha - r_f)\psi] r_f z}{(x^2 + z^2)^2} \, dz \qquad [16.19.29]$$

Horizontal target

$$F = \frac{2}{\pi} \int_h^{h+L} \frac{(x - r_f) r_f [x \sin \psi + (z \tan \alpha - r_f)\psi]}{(x^2 + z^2)^2} \, dz$$

Vertical target

[16.19.30]

where h is the height of the jet above the ground (including any lift-off), L is the visible length of the flame, $r_f(z)$ is the radius of the flame at height z, x is the distance between the axis of the jet and the target, z is the height of the flame differential element, α is the half-angle of the flame and $\psi(z)$ is the angular position of the flame differential element.

In the model of Chamberlain (1987) for a flare, the jet flame is treated as a frustrum with the widest end furthest from the jet exit, as shown in Figure 16.103. For

this case Crocker and Napier give the following expressions by Croce and Mudan (1986), in which the flame is treated as equivalent to a cylinder with diameter D_e and length L:

$$D_e = 2\frac{(W_1 + W_2)^{\frac{1}{2}}}{L}[L^2 + (W_2 - W_1)]^{\frac{1}{4}} \quad [16.19.31]$$

$$L = \frac{L_{BV} \sin \alpha_B}{\sin(90 - \alpha_B) \sin(180 - \theta)} \quad [16.19.32]$$

where the notation is as defined in Section 16.18.6 and Figure 16.103, except that L_{BV} is the height of the centre of the flame tip above the level of the jet exit (m) and α_B is the angle between the vertical and the line joining the jet exit and the centre of the flame tip (°). In general, the angle α_B is not equal to the angle α_b as defined in Figure 16.103, although the two become the same for a vertical jet. The view factor for this equivalent tilted cylinder is then obtained using the standard view factors for a tilted cylinder, as described in Section 16.17.

Crocker and Napier also give the results of a numerical investigation of the values of the radiation intensity on a target for a propane jet flame burning at a vent, as obtained for vertical and tilted flames using for the vertical flame the model of Hawthorne, Weddell and Hottel and the Becker relations, and for the tilted flame a point source treatment based on the model of Brzustowksi and Sommer, a multiple point source treatment based on the model of de Faveri *et al.* and the solid flame model of Chamberlain with the Croce and Mudan view factor. They select the latter as the preferred model for a tilted flame.

A treatment of the view factor for a jet flame is also given in the IP *LPG Storage Code*. To the extent that a jet flame may be characterized as a cylinder, view factors for cylinders may be used. The *Code* gives view factors for vertical and tilted cylinders with target levels above and below.

16.19.17 Application of models

The model of Hawthorne, Weddell and Hottel was used in some early work. For example, Gugan (1976), in a discussion of the release at Flixborough, expressed the view that whilst this model had not been verified for large-scale situations, there was no fundamental reason why it should not apply, and stated that use of the model to correlate incidents had not revealed any defect.

The model of Considine and Grint of SRD has been widely used by the HSE and others in hazard assessment work. The model is given in the CCPS *QRA Guidelines* (1989/5).

The Chamberlain model has been used by Shell for the study of possible impingement of jet flames from gas risers on the accommodation modules of oil production platforms, as described by Chamberlain (1989) at the Piper Alpha Inquiry.

The IP *LPG Storage Code* recommends for a jet flame of LPG the use of the Brzustowski and Sommer point source model provided that: (a) the target is at least one flame length away; (b) the fraction of heat radiated is taken as 0.38 for exit velocities up to Mach 0.5 and 0.22 up to Mach 0.9; (c) allowance is made for attenuation due to atmospheric transmittance; and (d) the code calculation methods are used. The flame length is taken as twice the distance from the flame centre to the point of discharge.

For the case where the target is less than one flame length away, the *Code* refers to the treatment of Chamberlain, whilst stating that this is not universally accepted.

16.19.18 Enclosed jet flames

The work just described relates to jet flames in the open. In some instances, a jet flame may occur within an enclosure. This case is of particular relevance to ignited releases in offshore modules.

Work on this aspect has been described by Chamberlain (1994). The experiments were conducted in an enclosure 8 m long × 3.54 m wide × 3.91 m high. The enclosure contained a cylindrical target 0.27 m in diameter, and thermocouples, radiometers and total heat flux gauges were located on the target and the enclosure walls. Propane was released both as a vapour, in the subsonic and sonic flow regimes, and as a liquid at a flow which averaged 0.21–0.3 kg/s. Both vertical and horizontal nozzle orientations were used. Some trials were conducted with full end wall opening and others with partial wall opening (2.5 m × 2 m); one trial condition involved a partially open roof. Measurements were also made of the composition, particularly the carbon monoxide concentration, of the combustion products and of the size of and thermal radiation from the external flame from the enclosure.

The situation investigated is strongly similar to the compartment fires which have been much studied in work on fires in buildings, as described in Section 16.36. In the ventilation-controlled conditions which occur in a compartment the hot combustion products flow out through the top of the aperture and cold air flows in through the bottom, with a relatively well-defined boundary between the two. This has led to the three zone model of a compartment fire, the three zones being the fire plume itself and the hot and cold gas zones. The air flow in such a fire is normally modelled in terms of the ventilation factor $AH^{\frac{1}{2}}$, where A is the area of the ventilation opening (m^2) and H is its height (m).

However, a jet flame in an enclosure differs from the pool fire case in at least two important respects. One is the much greater degree of mixing and the other the absence of 'flashover'.

Some of the findings from these tests were as follows. For ventilation-controlled fires with vertical apertures it took about 10 minutes to reach steady-state conditions. The boundary between the hot and cold layers occurred about halfway up the opening. The gas temperature in the upper layer was remarkably uniform and could reach about 1200°C.

In addition to the heat effects on the wall and the contents of the enclosure, other hazards are the thermal radiation from the external flame and the generation of smoke and carbon monoxide.

In some tests using propane gas from a vertical nozzle the heat flux at the impingement area on the roof reached over 300 kW/m^2, rising to this value as radiation from the walls came into play.

For the external flame the maximum vertical and horizontal extents measured were 6 and 3 m, respectively, for a trial using liquid propane, though two trials using propane gas gave comparable values of 5 and 3 m,

respectively; there was no external flame in the two trials with full wall opening.

It is the flame stoichiometry which governs the production of soot and carbon monoxide. This stoichiometry is a function of the fuel flow, the jet momentum and the vent opening. The experiments showed that the parameter $0.5AH^{\frac{1}{2}}$ tends to give an overestimate of the air flow. The author advises against its use for the determination of flame stoichiometry.

Jet flames which were fuel rich gave much higher yields of soot and of carbon monoxide and larger external flames.

When ventilation-controlled, roof ventilated jet flames were found to be unstable and to self-extinguish. With this geometry a stable two-way flow of air and combustion products is not established.

16.20 Engulfing Fires

The engulfment of vessels in fire may occur in various ways and the problem has been studied from several different angles. Important distinctions relate to the container, which may be a fixed tank or vessel or pipework or a transport container, and to the fire, which may be a pool fire or a directed flame.

There have been a number of experiments on rail tank cars and on fixed storage vessels engulfed in fire, and various models have been developed for heat transfer to such vessels, for the response of the temperatures and pressures in the vessel, for pressure relief of the vessel and for bursting of the vessel. Some studies of engulfing fires are given in Table 16.71.

16.20.1 Heat absorbed

Relations for the heat absorbed by a vessel from a pool fire are given in API RP 520: 1976 *Recommended Practice for Design and Installation of Pressure Relieving Systems in Refineries* and API Std 2000: 1982 *Venting Atmospheric and Low-pressure Storage Tanks*. It is convenient to consider first the relationships given in these publications and then the subsequent changes.

The two documents mentioned give for the heat absorbed by the wetted surface area expressions of the general form

$$Q = kA^n \qquad [16.20.1]$$

where A is the wetted surface area, Q is the heat absorbed, k is a constant and n is an index.

For the estimation of the heat absorbed for purposes of determining relief requirements, API RP 520 gives the equation

$$Q = 21\,000\,FA^{0.82} \qquad [16.20.2]$$

where A is the wetted area (ft^2), F is an environment factor and Q is the heat absorbed (BTU/h).

API RP 520 contains an appendix (Appendix A) in which the origin of Equation 16.20.2 is explained. It is based on tests carried out in 1925 by Standard Oil of California. The tests were conducted on a small tank and were intended to give guidance on relief sizing for tank trucks. The tests indicated the maximum heat absorption rate to be expected in the worst case. There were also available data on cases where tanks had survived fire exposures. The available data were plotted by Stroop on log–log paper as a curve. This curve was intended to give guidance for small tanks and, by extrapolation, for tanks with wetted areas up to $10\,000\,ft^2$. It was subsequently observed by Maker that the data could be represented by a straight line and he proposed the equation

$$q = 48\,000\,A^{-\frac{1}{3}} \qquad [16.20.3]$$

where q is the heat absorbed per unit area ($BTU/h\,ft^2$) and A is the wetted area (ft^2). Equation 16.20.3 became known as the Stroop–Maker formula and was applied not only to atmospheric storage tanks but also to pressure vessels.

Another set of equations developed during the Second World War are the formulae of the Petroleum Administration for War (PAW). These are

$$q = 16\,000\,A^{-0.18} \qquad [16.20.4]$$

$$Q = 16\,000\,A^{0.82} \qquad [16.20.5]$$

The Stroop–Maker and PAW formulae have been widely used in the petroleum industry.

Table 16.71 *Some studies of engulfing fires*

Derivation of formulae for heat absorbed by a vessel exposed to fire	API RP 520: 1976; API Std 2000: 1982
Experiment on fire engulfment of a full scale rail tank car vessel containing LPG	C. Anderson *et al.* (1974); Charles (1974)
Discussion of heat absorbed in fire engulfment	Craven (1976)
Experiments on fire engulfment of $\frac{1}{5}$ scale rail tank car vessels containing LPG	Appleyard (1980)
Experiments on fire engulfment of small and full scale vessels containing LPG	A.F. Roberts, Cutler and Billinge (1983); Moodie, Billinge and Cutler (1985)
Theoretical studies of temperatures and pressures in vessels and pipes containing gas or liquid engulfed by fire	Solberg and Borgnes (1983)
Theoretical studies of temperatures and pressures in a vessel filled with gas engulfed by fire	Nylund (1984)
Theoretical models for heat transfer from pool fires and jet fires (relief valve flare) to a horizontal cylinder	Tunc and Venart (1984/85a,b)
Theoretical model of temperatures and pressures in a vessel containing liquid engulfed by fire	D.L.M. Hunt and Ramskill (1985)

API RP 520 gives a plot comparing the PAW and API formulae given here as Equations 16.20.2 and 16.20.5, respectively, with various additional data points obtained from tests carried out during the period 1925–1950. Some of the tests represent the worst conditions likely to occur, since they were delayed until calm conditions prevailed and plentiful fuel supplies were used.

API Std 2000 quotes Equation 16.20.2 for use in determining the venting requirements of atmospheric and low pressure storage tanks for wetted areas greater than 2800 ft^2. It also gives tables for determining the venting requirements for wetted areas less than this. It is explained in an appendix (Appendix B) that the tables are based on the following equations:

$$Q = 20\,000\,A \qquad 20 < A < 200 \qquad [16.20.6a]$$

$$Q = 199\,300\,A^{0.566} \qquad 200 < A < 1000 \qquad [16.20.6b]$$

$$Q = 963\,400\,A^{0.338} \qquad 1000 < A < 2800 \qquad [16.20.6c]$$

The method used in earlier versions of API Std 2000 was to assume a constant value of heat absorbed ($q = 6000$ BTU/h ft^2), but tests conducted in 1961 on a horizontal tank led to a revision and development of the equations just quoted.

A discussion of the heat absorbed by a vessel in an engulfing fire has been given by Craven (1976). He suggests that if a well developed fire radiates heat at a given rate, then it could be argued that an object engulfed in a fire should receive heat at the same rate, since the view factor is unity. A large fire can radiate heat at a rate of some 17 W/cm^2 (170 kW/m^2). In tests on small tanks the heat input rates recorded are, on average, about 11 W/cm^2 (110 kW/m^2), while for large tanks they rarely exceed 7 W/cm^2 (70 kW/m^2). The exponents in Equations 16.20.1, as given in Table 16.72, reflect this falling off in heat absorption with size. Craven argues, however, that there is no theoretical justification for an exponent less than unity and that in certain circumstances a vessel might receive a heat input nearer 17 W/cm^2 (170 kW/m^2). For the latter case he gives the equation

$$Q = 54\,000\,A \qquad [16.20.7]$$

where A is the wetted area (ft^2) and Q is the heat absorbed (BTU/h).

Figure 16.109 (Crawley and Scott, 1984) shows a comparison of the PAW and API formulae and some of the data points given in API RP 520.

The history of the API RP 520 treatment of heat absorption is discussed by Heller (1983).

API RP 520: Part 1: 1990 gives in Appendix D two equations for the heat absorbed, which differ in that they are based on the adequacy of drainage and fire protection. The first is Equation 16.20.2 and the second the equation

$$Q = 34\,500\,FA^{0.82} \qquad [16.20.8]$$

Equation 16.20.2 is to be applied where adequate drainage and fire-fighting equipment exist and Equation 16.20.8 where they do not.

The API recommendations are therefore as follows. API RP 520: 1990 and API Std 2000: 1992 recommend the use of Equation 16.20.1 with the constants shown in Table 16.72.

It should be borne in mind that the API RP 520 equations are given for the purpose of plant design rather than hazard assessment.

Further information on the heat absorbed is given below in relation to particular studies of engulfing fires.

16.20.2 General studies of engulfing fires

A series of theoretical studies of the effect of engulfing fires on vessels and pipework with and without insulation has been carried out by Borgnes, Solberg and co-workers, as reported by Solberg and Borgnes (1983). The work was done using the Det norske Veritas (DnV) computer program NV613 for the determination of temperature profiles.

The heat absorbed in an engulfing fire is not well defined, but at the flame surface a heat flux of about 150 kW/m^2 seems to be a reasonable value. Inside the flame the heat flux would be higher; how much higher is uncertain, but perhaps by some 50–100 kW/m^2. There is also a convective heat flux. For pool fires a heat flux of 30–40 kW/m^2 is a conservative estimate, but for jet fires it may be appreciably higher. The approach taken is therefore as follows. Heat transfer is assumed to be by radiation only, with the object engulfed in the flame so that the view factor is unity. The flame temperature of the engulfing fire is assumed to be 1525 K with the flame emissivity and target absorbtivity both taken as unity. The justification for the latter is that in such a fire the metal would soon be covered with a deposit of carbon. For an object at an initial temperature of 400 K the initial heat flux under these conditions is 310 kW/m^2.

The temperature at which steel suffers serious loss of strength, or the critical steel temperature, is taken as 675 K.

The base case is a considered 2 m diameter vessel with 20 mm wall thickness and 50 mm mineral wool insulation, containing gaseous propane at an initial

Table 16.72 *Parameters for use in the equations given in API RP 520 and API Std 2000 for the heat absorbed in fire engulfment*

	Wetted area, A		*Heat absorbed,* Q		*Conditions*
	(ft^2)	(m^2)	(BTU/h)	(kW)	
API RP 520: 1990			$21\,000A^{0.82}$	$43.1A^{0.82}$	–[a]
			$34\,500A^{0.82}$	$70.8A^{0.82}$	–[b]
API Std 2000: 1992	20–200	1.86–18.6	$20\,000A$	$6.31A$	
	200–1000	18.6–92.9	$199\,300A^{0.566}$	$224.1A^{0.566}$	
	1000–2800	92.9–260	$963\,400A^{0.338}$	$632.0A^{0.338}$	
	>2800	>260	$21\,000A^{0.82}$	$43.1A^{0.82}$	

[a] Drainage and fire fighting equipment adequate.
[b] Drainage and fire fighting equipment inadequate.

temperature of 400 K and at pressures of 5, 20 and 80 bar. Figure 16.110(a) shows the wall temperatures attained for different gas pressures after different time periods. For an uninsulated vessel the critical steel temperature is reached within a few minutes. For an insulated vessel at 5 bar pressure the time to critical steel temperature is less than 1.5 h, while for one at 80 bar pressure the steel reaches a temperature of 610 K after 2 h.

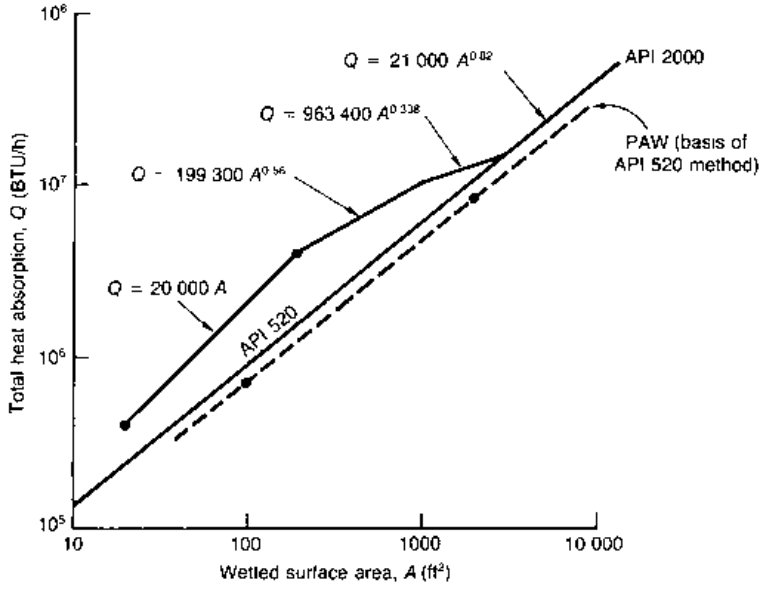


Figure 16.109 *Comparison of the equations given by the API for the heat absorbed by a tank or vessel in a fire (Crawley and Scott, 1984) (Courtesy of the Institution of Chemical Engineers)*

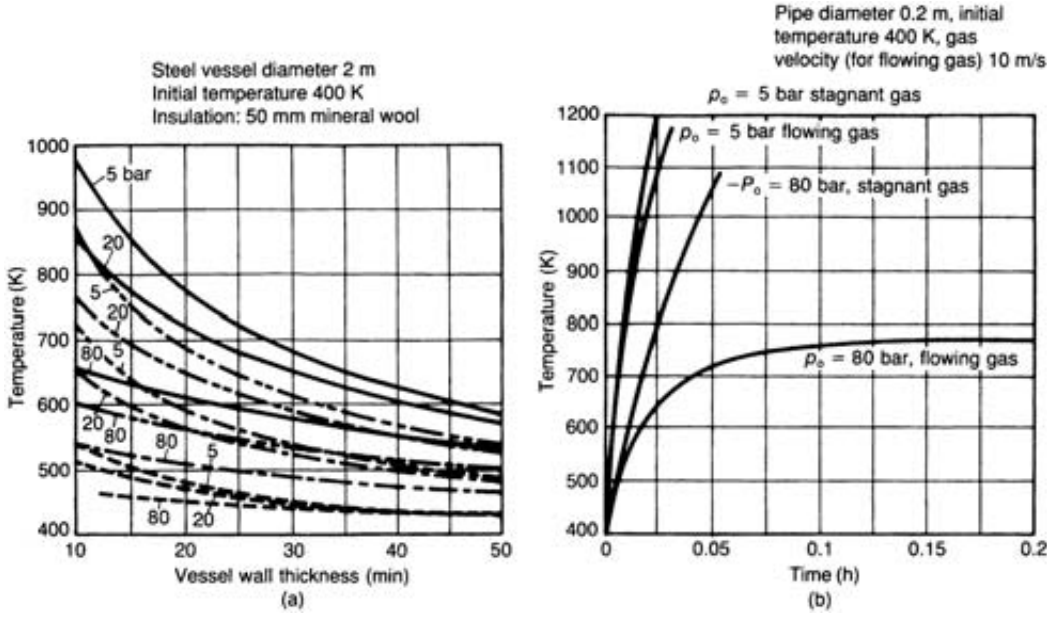
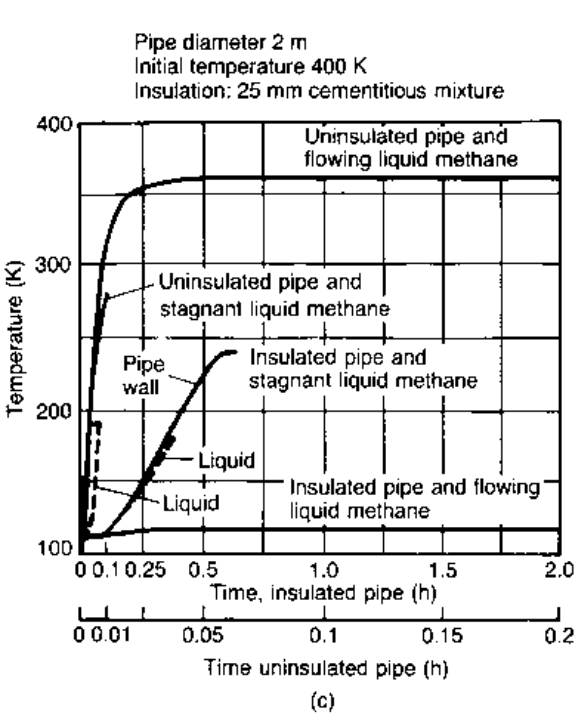
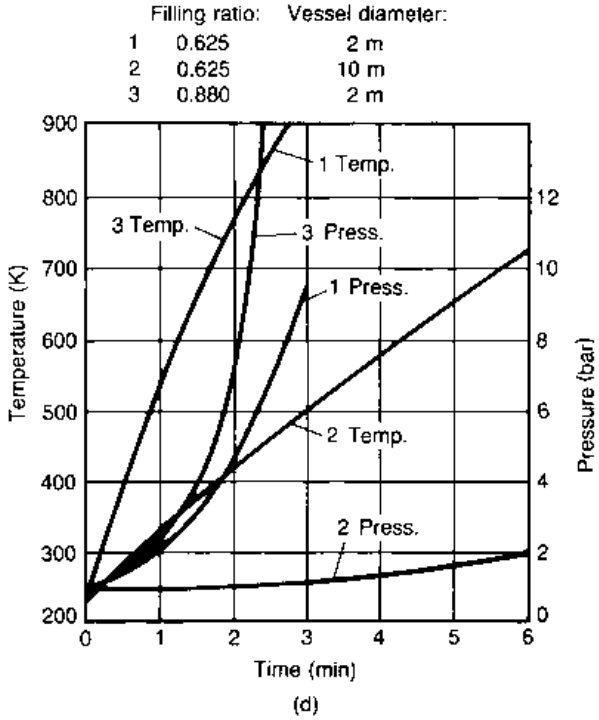
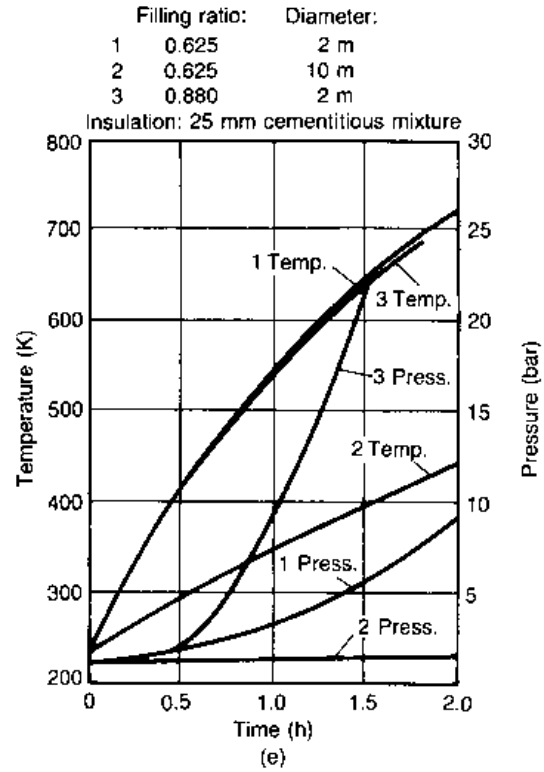


Figure 16.110 *Theoretical predictions of the temperatures and pressures in vessels and pipes containing gas and liquids engulfed in a fire (after Solberg and Borgnes, 1983). (a) temperature rise of the outside of the vessel wall for vessel filled with propane gas; (b) temperature rise of the pipe wall (uninsulated) for pipe filled with stagnant and flowing methane gas; (c) temperature rise of the pipe wall (uninsulated and insulated) for pipe filled with stagnant and flowing liquid methane; (d) maximum outside vessel wall temperature and pressure in uninsulated vessel for vessel partly filled with liquid propane; (e) maximum vessel wall temperature and pressure in insulated vessel partly filled with liquid propane; (f) temperature profile of insulated vessel wall for vessel partly filled with liquid propane. (Courtesy of the American Institute of Chemical Engineers)*

Figure 16.110 *Continued*







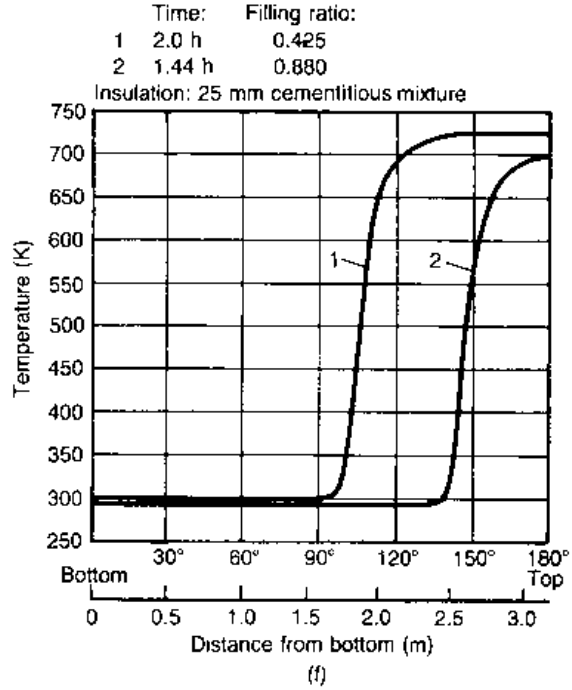


Figure 16.110(b) shows, for a 0.2 m diameter uninsulated pipe, the times to different wall temperatures for stagnant and flowing methane gas at 5 and 80 bar pressure. Figure 16.110(c) shows, for uninsulated and insulated pipe of the same diameter, the wall temperature response for stagnant and flowing liquid methane at an initial temperature of 110 K.

Figure 16.110(d) shows the wall temperature and gas pressure responses for 2 and 10 m uninsulated horizontal vessels partly filled with liquid propane, with fill ratios of 0.625 and 0.88. Figure 16.110(e) shows the corresponding responses for insulated vessels. For the latter case the temperature profile in the vessel wall is shown in Figure 16.110(f). This very steep temperature gradient may give rise to severe stresses in the vessel shell.

The authors also describe work on other aspects, such as the effect of defects in the insulation and unevenness in water sprays.

16.20.3 Vessels filled with gas

A theoretical study of the effect of an engulfing fire on a vessel filled with methane has been made by Nylund (1984). The vessel considered was 13 m long × 3 m diameter with a wall thickness of 53 mm, a working temperature of 300 K and a pressure of 8.2 MPa.

Pool and jet fires were investigated. The flame temperature for both fires was assumed to be 1500 K. The convective heat transfer coefficient was taken as 28 W/m^2K for the pool fire and as 250 W/m^2K for the jet fire. A model is given for vessel rupture as a function of vessel temperature and pressure and wall thickness.

Some of the results obtained by Nylund are shown in Figure 16.111. Figure 16.111(a) shows the time response of the gas temperature, the gas pressure and the rupture pressure for a jet fire, for a jet with an effective diameter of 1 m. The rupture pressure does not fall below the gas pressure. Figure 16.111(b) shows the response for a jet fire with a jet having an effective diameter of 4 m. In this case the rupture pressure does fall below the gas pressure, so the vessel would rupture. Rupture is predicted for jet fires with jets having an effective diameter of 2, 3 and 4 m for which the pressure crossovers occur at about 7.5, 7 and 5 minutes, respectively. Figure 16.111(c) shows the response for a pool fire. In this case not only does the rupture pressure fall, but the gas pressure rises appreciably so that rupture occurs in somewhat less than 5 minutes.

Nylund also discusses pressure relief and depressurization. In both types of fire rupture can occur within 5 minutes. For neither type does a pressure relief valve provide real protection. In the case of the jet fire the rupture occurs at gas pressures well below the relief valve set pressure. In the pool fire case the gas pressure does reach the set pressure, but the relief valve capacity is insufficient to vent the pressure quickly enough.

Depressurization is capable of providing protection. Figure 16.111(d) illustrates a successful depressurization.

16.20.4 Vessels part filled with liquid

There have been several experimental investigations of the response of vessels containing liquefied flammable gas to an engulfing fire.

A test on fire engulfment of a 64 te LPG rail tank car has been described by C. Anderson *et al.* (1974) and Charles (1974). Measurements were made of the heat flux from the fire, of the vessel wall temperatures in the liquid and vapour spaces and of the relief valve flare. The relief valve opened at 1.96 MPa and remained open. The vessel ruptured after some 24.5 minutes, propelling 63 fragments, some for considerable distances. The pressure at failure was 24.1 bar and the wall temperature near the point where failure occurred had a maximum value of 650°C. The temperatures of and heat fluxes from the pool fire and the relief valve torch are given in Table 16.73.

A series of tests on vessels for rail tank cars have been carried out at $\frac{1}{5}$ scale by Appleyard (1980). One objective of these tests was to investigate the effectiveness of the internal thermal radiation protection Explosave.

These and other tests have been reviewed by Tunc and Venart (1984/85b) and by Moodie, Billinge and Cutler (1985).

Models for radiant heat transfer to a horizontal cylindrical vessel from (1) an engulfing fire and (2) a relief valve flare have been given by Tunc and Venart (1984/85a,b).

Large scale tests on the effect of fire around a liquid ethylene storage vessel have been carried out as part of the experiments by the MITI (1976) described earlier.

In one test, a storage vessel with vacuum perlite insulation fitted with a 25 cm diameter bursting disc and containing 718.5 kg of liquid ethylene was subjected to a flame from LPG burners for 15 minutes with the water sprays on and then for 15 minutes with the sprays off. The total quantity of LPG consumed in the fire was 80 kg and the total heat released was estimated as 960 000 kcal. The pressure in the vapour space in the vessel remained at about 1.0 kg/cm^2g throughout the test.

In another test the insulating vacuum of the vessel was broken and part of the perlite at the base of the vessel was removed. The vessel was subjected to a pool fire of kerosene which engulfed it. The water spray was not used on the vessel. The total quantity of heat released by the kerosene fire was estimated as 34 496 000 kcal. The bursting disc blew when the vapour pressure reached 8.3 kg/cm^2g, which occurred 34 minutes after ignition.

When the disc blew, some 620 kg of ethylene was ejected as a vapour–liquid mixture within about 6.5 seconds. The material ignited and gave a large flame which lasted about 8–9 seconds and was about 100 m long. The actual length of the flame agreed well with the value of 105 m calculated from Equation 16.19.21 assuming that 620 kg was released over 8 seconds.

Part of the flame formed a fireball. The diameter and duration of the fireball were calculated from the NASA formula (Equations 16.16.5 and 16.16.7). The total mass of the combustion reactants was taken to include the air required for combustion, so that 28 kg of ethylene require 96 kg of oxygen, making a total mass of 124 kg. The observed fireball had a diameter of 40 m and persisted for about 3 seconds. According to Equations 16.16.5 and 16.16.7 this corresponds to about 324 kg of ethylene. Thus on the basis of this calculation about half the mass of ethylene ejected was involved in the fireball.

Two series of tests on horizontal cylindrical vessels partly filled with liquid and engulfed in a pit fire have been carried out by the HSE. In the first series, described by A.F. Roberts, Cutler and Billinge (1983),

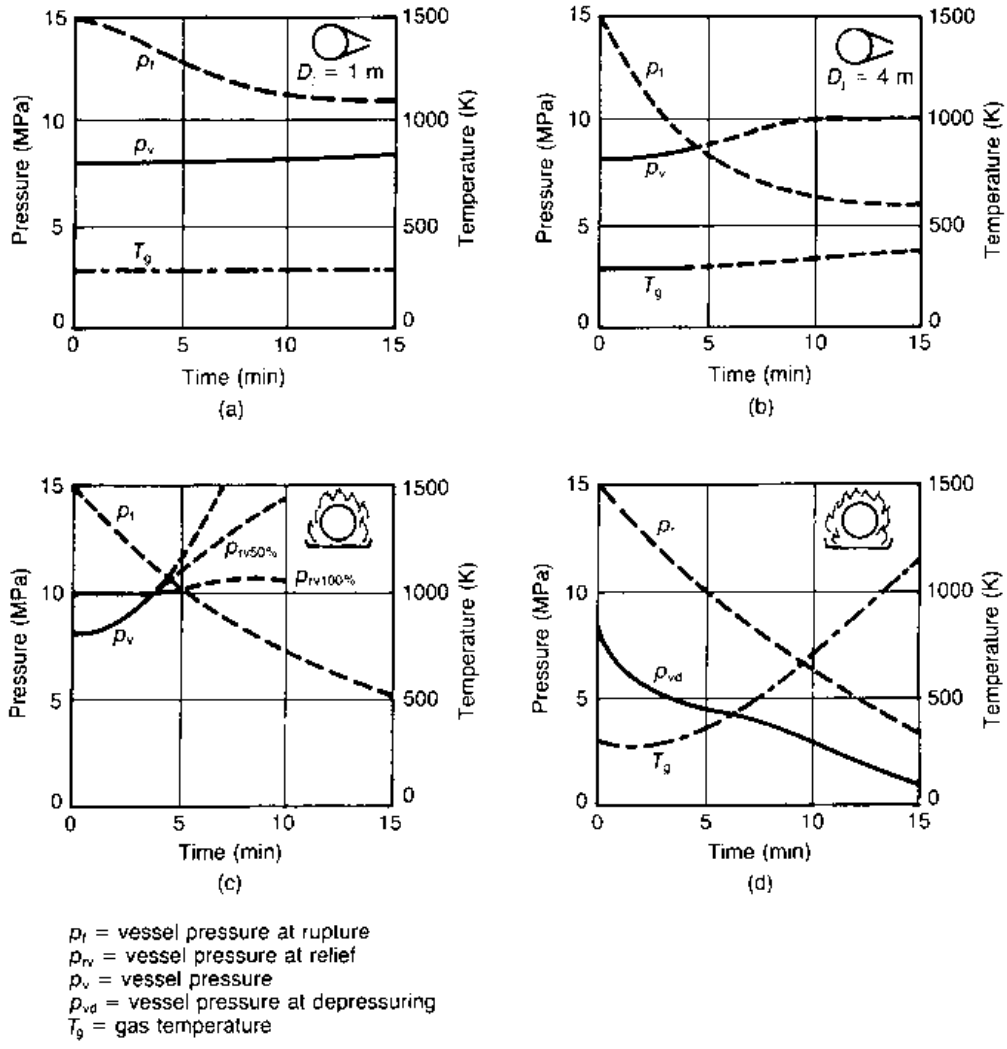


Figure 16.111 *Theoretical predictions of the temperatures and pressures in vessels filled with gas (after Nylund, 1984): (a) impingement of jet flame 1 m diameter; (b) impingement of jet flame 4 m diameter; (c) engulfing fire; (d) engulfing fire with depressurization (Courtesy of the Institution of Chemical Engineers)*

Table 16.73 *Temperatures and heat fluxes in a full scale fire engulfment test on a rail tank car (Tunc and Venart, 1984/85b; after Charles, 1974) (Courtesy of the* Fire Safety Journal*)*

Time (min)	*Recorded heat flux* (kW/m^2)	*Temperature* (°C)		*Heat flux* (kW/m^2)	
		Fire	*Torch*	*Fire*	*Torch*
5.0–11.5	90.12	871	1120	60.28	171.8
11.5–15.0	68.7	816	1040	49.4	134.28
15.0–24.5	29.65	802	1090	46.94	159.22
Maximum reading (6.5 min)	104.8	871	1180	60.28	203.4

Table 16.74 *Experimental conditions and heat fluxes in fire engulfment tests on vessels containing propane (after Moodie, Billinge and Cutler, 1985) (Courtesy of the Institution of Chemical Engineers)*

Test	*Tank size* (te)			
	$\frac{1}{4}$	$\frac{1}{4}$	1	1
Degree of fill (%)	40	80	40	20
Mass of liquid (kg)	100	870	420	160
Volume of liquid (m^3)	185	1635	789	308
Tank pressure (bar)	5.5	6.1	4.1	4.1
Ambient temperature (°C)	5	14	−3	−3
Surface areas (m^2):				
Total	3.8	10.4	10.4	10.4
Wetted	1.68	6.28	4.32	3.02
Average heat flux (kW/m^2):				
To propane before venting	73	84	59	33
To walls before venting	24	34	16	28
To propane during early stages of venting	85	50	54	76

5001 vessels were used. A preliminary set of tests was done with vessels containing water; the main tests were then done with LPG.

In the tests using water the vapour space heated up rapidly and caused boiling at the water surface at 4 minutes. The bulk water began to boil after 8 minutes. Between 4 and 8 minutes the boiling reduced the temperature of the vapour but not that of the wall in the vapour space. After 8 minutes it reduced both these temperatures.

The heat balance on the wall was expressed as

$$\rho c d \frac{\mathrm{d}T_1}{\mathrm{d}T} = Q - \epsilon\sigma T_1^4 - \sigma \mathrm{F} T_1^4 \qquad [16.20.9]$$

where the second and third terms on the right-hand side represent the heat radiated externally and that radiated internally, respectively. The equation is solved to give

$$\frac{4Qt}{\rho c d T_\mathrm{A}} = \ln\left(\frac{T_\mathrm{A}+T_1}{T_\mathrm{A}-T_1}\right) - \ln\left(\frac{T_\mathrm{A}+T_\mathrm{o}}{T_\mathrm{A}-T_\mathrm{o}}\right) + 2\tan^{-1}\left(\frac{T_1}{T_\mathrm{A}}\right) - 2\tan^{-1}\left(\frac{T_\mathrm{o}}{T_\mathrm{A}}\right) \qquad [16.20.10]$$

with

$$T_\mathrm{A} = \left[\frac{Q}{\sigma(\epsilon+F)}\right]^{\frac{1}{4}} \qquad [16.20.11]$$

where c is the specific heat of the wall metal, d is the thickness of the metal wall, F is a factor (explained below), Q is the heat absorbed per unit area, T_A is the asymptotic value of T_1, T_o is the initial value of the wall temperature, T_1 is the value of the wall temperature at time t, ϵ is the emissivity of the external surface of the wall, ρ is the density of the metal and σ is the Stefan–Boltzmann constant. The factor F includes the emissivity of the internal surface of the wall, the absorptivity of the water surface and the view factor from the wall to the water surface.

Equation 16.20.10 was used to obtain estimates of the heat absorbed Q and of the factor F from the wall temperature data. The heat absorbed was estimated to have an average value of $134\,kW/m^2$ and the factor F a value of 0.055, which is consistent with a wall emissivity of unity, a water surface absorptivity of 0.09 and the view factor of $2/\pi$. The estimated average flame temperature was 1100°C.

The calculated equilibrium conditions for the unwetted upper part of the vessel were a wall temperature of 950°C, a total heat transfer from the fire of $134\,kW/m^2$, re-radiation from the vessel to the atmosphere of $127\,kW/m^2$ and internal radiation to the liquid layer $7\,kW/m^2$. For the wetted lower part of the vessel the total heat transfer was estimated as $124\,kW/m^2$, giving an overall average heat flux of $130\,kW/m^2$.

The main set of ten trials were then conducted using propane, one with an uninsulated vessel and nine with insulated vessels. A feature of these trials was the behaviour of the pressure relief valves. The valves were set to open at 1.7 MPa, but in fact opened at pressures in the range 0.7–1.8 MPa, due probably either to weakening of the spring or damage to the valve seat from the effects of the fire.

In the water tests the boiling regime was nucleate boiling. In the propane tests the regime was film boiling in most cases, although nucleate boiling did occur. Figure 16.112(a) illustrates film boiling in which the wall temperature in the liquid space is close to that in the vapour space, while Figure 16.112(b) shows nucleate boiling when the liquid space wall temperature is much lower. The occurrence of film boiling, and the associated poor heat transfer, therefore renders the walls vulnerable to thermal weakening.

In the second series of fire engulfment tests by the HSE, described by Moodie, Billinge and Cutler (1985) the tanks used were $\frac{1}{4}$ and 1 te uninsulated vessels part filled with propane. Five tests were carried out, two with $\frac{1}{4}$ te vessels and three with 1 te vessels. In one of the former tests the pressure relief valve failed, so that there were four successful tests. Plate 13 shows a test in which the pressure relief valve is operating, giving a large jet flame.

The vessels were instrumented for the measurement of temperatures in the tank wall, the vapour space and the liquid, as shown in Figure 16.113.

In these larger scale tests the fire was deficient in oxygen and gave a yellow, smoky flame. The flame temperatures were 900–950°C with a maximum of 1000°C. The maximum wall temperatures recorded were in the range 600–800°C, which is consistent with a flame emissivity of 0.56.

The experimental conditions and heat fluxes are summarized in Table 16.74.

Thus in the successful $\frac{1}{4}$ te tank test the average heat flux before venting into the propane was estimated as

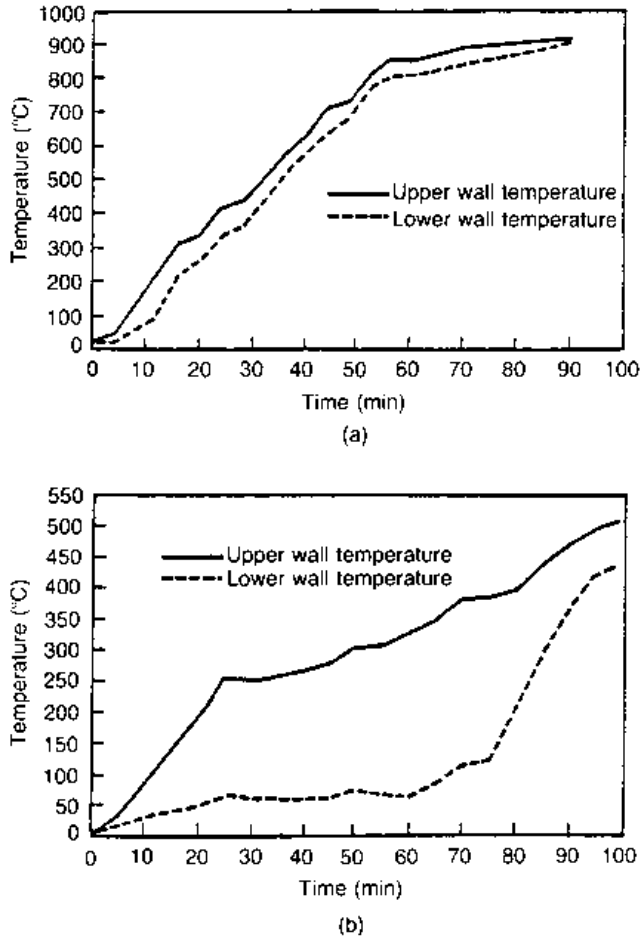


Figure 16.112 *Temperatures in a 500 l vessel part filled with propane engulfed in fire (A.F. Roberts, Cutler and Billinge, 1983): (a) typical film boiling; (b) typical nucleate boiling (Courtesy of the Institution of Chemical Engineers)*

73 kW/m^2 and that into the tank wall as 24 kW/m^2, giving a total of 97 kW/m^2. During venting the heat flux into the propane was 80 kW/m^2.

The four successful tests, one with the $\frac{1}{4}$te tank and three with the 1 te tank, showed a similar pattern. The wall temperature of the vapour space rose almost linearly, while the wall temperature of the liquid space rose to a plateau, levelled out and then rose again. When the pressure relief valve opened giving a nearly constant pressure the liquid wall temperature settled just above the corresponding boiling point, until the wall became exposed due to evaporation of the liquid. Figure 16.114(a) shows for the successful $\frac{1}{4}$te test the temperatures of the walls in the liquid and vapour spaces and Figure 16.114(b) shows the temperatures of the vapour and liquid.

The behaviour of the wall temperature in the liquid space in these tests points to nucleate rather than film boiling, and estimates of the heat flux indicate that the high heat fluxes necessary for film boiling did not occur.

In all the successful tests the internal pressure rose to the relief valve set pressure within 3–5 minutes. The relief valves cycled at least twice, then remained open venting the pressure down eventually to atmospheric pressure. This behaviour was attributed to weakening of the springs or damage to the seats due to the fire. Although the vessel walls would be weakened by the high temperatures experienced, at no time did the internal pressure have a value which would have been likely to cause rupture.

One of the tests on the $\frac{1}{4}$te tank with 40% fill was unsuccessful in that the relief valve, after opening

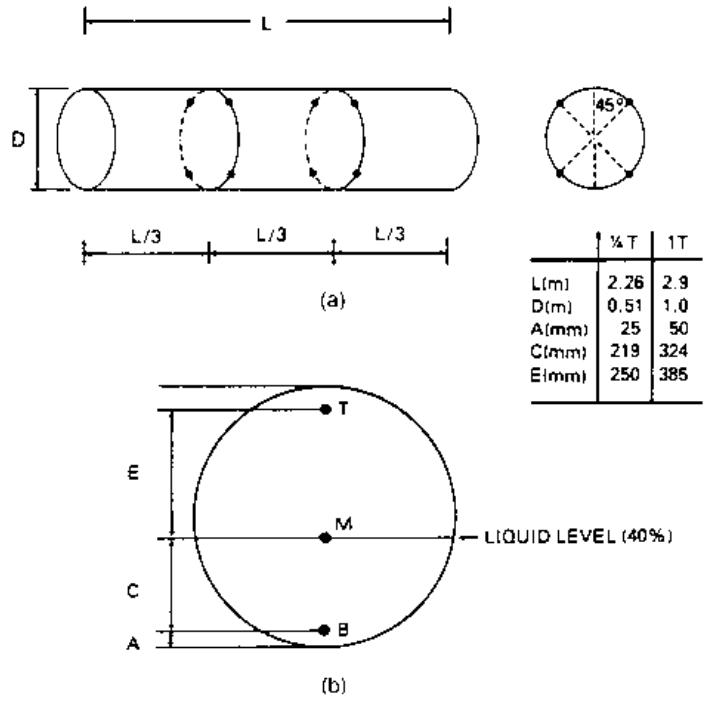


Figure 16.113 *Temperature measurement arrangements in fire engulfment tests on $\frac{1}{4}$ and 1 te vessels part filled with propane (Moodie, Billinge and Cutler, 1985): (a) positions of the wall thermocouples; (b) positions of the internal thermocouples (Courtesy of the Institution of Chemical Engineers)*

correctly, failed to do so subsequently. The vessel ruptured at an internal pressure of 35 bar and maximum wall temperature of 600°C.

Metallurgical examination revealed no indication of failure due to cracks and was consistent with failure by hoop stress in the wall. The authors suggest that the burst pressure may therefore be calculated from thick-walled cylinder theory and give the equation

$$P_b = \frac{2}{3^{\frac{1}{2}}}\sigma_y A \ln K \qquad [16.20.12]$$

with

$$A = 2 - \sigma_u/\sigma_y \qquad 0 < T < 700 \qquad [16.20.13a]$$

$$A = 1 \qquad T > 700 \qquad [16.20.13b]$$

where K is the ratio of the outside to the inside diameter, P_b is the burst pressure, T is the metal temperature (°C), σ_u is the ultimate tensile strength and σ_y is the yield strength, both as measured at temperature T.

If the wall temperature in this test is taken as 600°C, the burst pressure calculated by Equation 16.20.12 is 38 bar, which is within 8% of the observed value. Moreover, application of Equation 16.20.12 to data given by C. Anderson *et al.* (1974) and Droste *et al.* (1984) predicts all the burst pressures with an error of less than 18%. The authors also discuss the implications of the work for the pressure relief of vessels engulfed in fire.

In association with these tests a theoretical model for the behaviour of a vessel engulfed in fire has been developed by D.L.M. Hunt and Ramskill (1985). Figure 16.115 shows the heat flows taken into account in the model.

Some predictions given by the model for one of the 500l vessels in the first HSE series of tests are compared with the observed values in Figure 16.116. Figure 16.111(a) shows the wall temperatures of the vapour and liquid spaces and Figures 16.116(b) and (c) the temperatures of the vapour and liquid, respectively.

16.20.5 Jet flame attack

There is relatively little available data on the effect on equipment of jet flame attack, as opposed to pool fire engulfment, but the EC currently has in hand a major programme of work on this, an account of which is given by Duijm (1994). The objectives of the programme are (1) the modelling of unobstructed jet fires, (2) the modelling of obstructed jet fires, (3) the modelling of the thermal response of pressure vessels, (4) the assessment of mitigation techniques and (5) the modelling of the failure modes of the pressure vessels.

For unobstructed single-phase jet flames the work involves the development of the models incorporated in the UMPFIRE and TORCIA codes, as described by

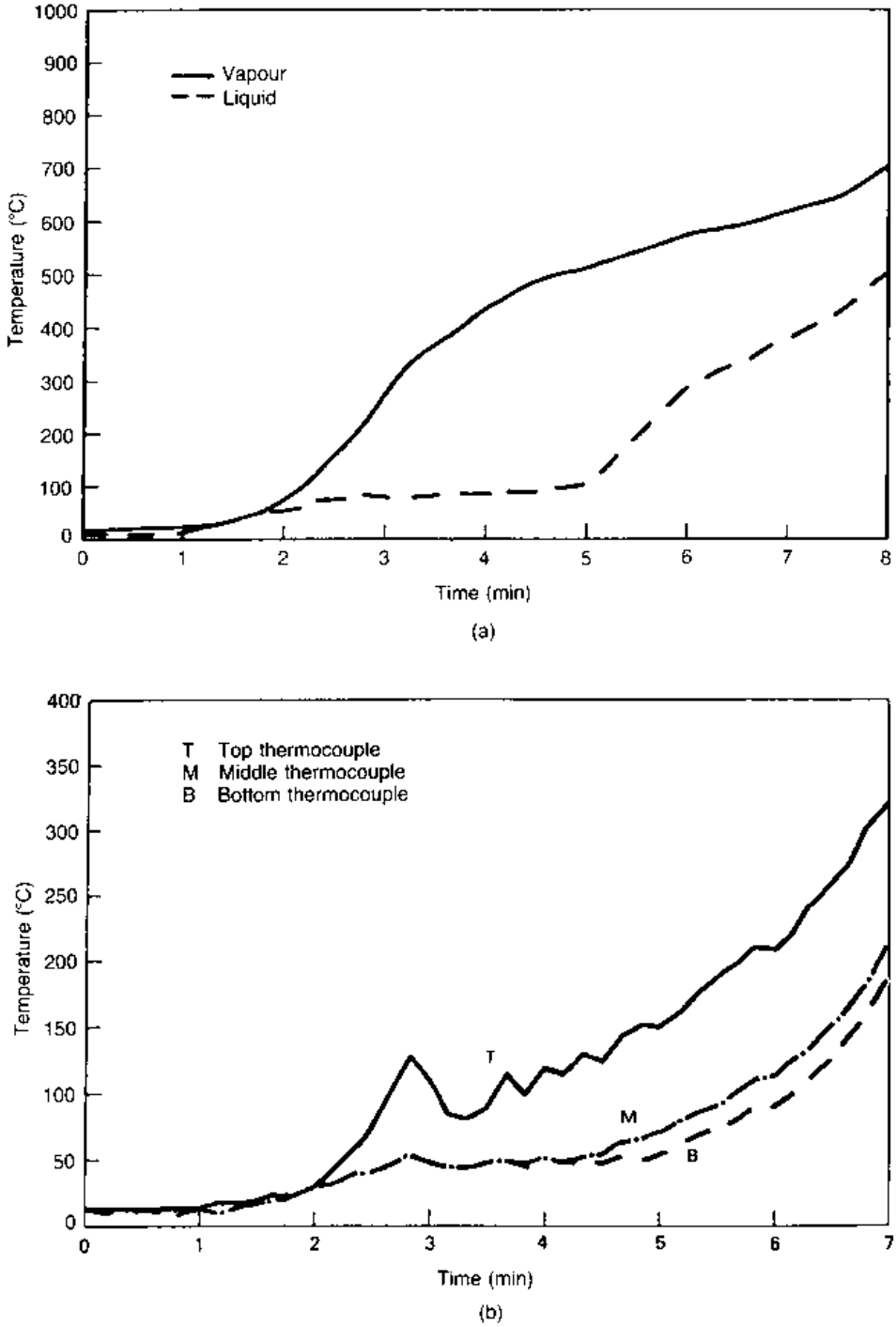


Figure 16.114 *Temperatures in the $\frac{1}{4}$te vessel part filled with propane engulfed in fire (Moodie, Billinge and Cutler, 1985): (a) temperatures of walls in liquid and vapour spaces; (b) temperatures of vapour and liquid (Courtesy of the Institution of Chemical Engineers)*

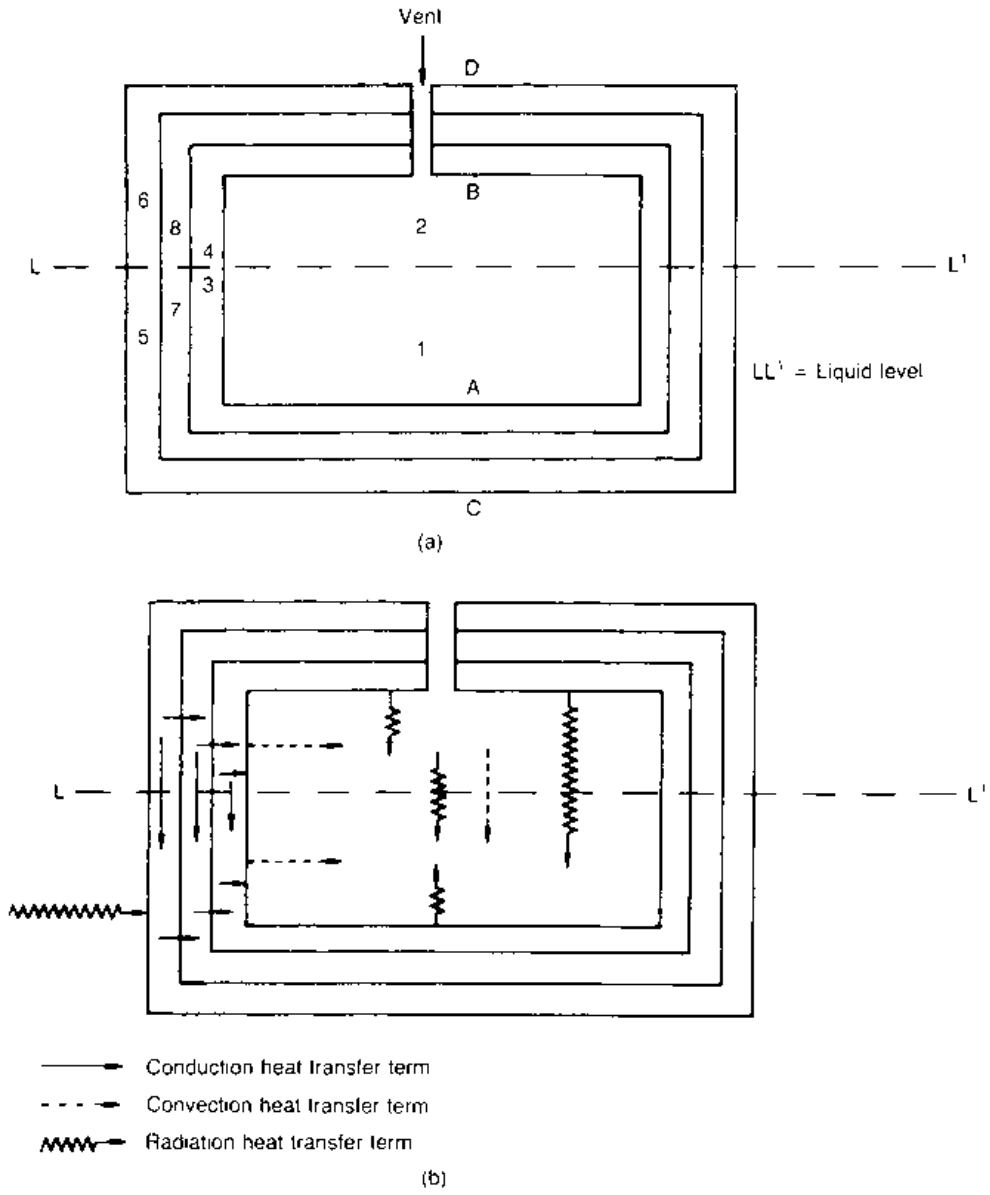


Figure 16.115 *Heat flows in the theoretical model of heat transfer in a vessel engulfed in fire (D.L.M. Hunt and Ramskill, 1985): (a) the tank node scheme; (b) heat transfer within the tank (Courtesy of the Institution of Chemical Engineers)*

Crespo *et al.* (1991) and Bennett *et al.* (1991), with extension of the treatment to two-phase jet flames. For obstructed jet flames a distinction is made between small targets engulfed by the flame and large targets. For the latter the heat flux distribution can be very non-uniform and can thus create thermal stresses. The heat fluxes shown in the figures given by Duijm vary between 40 and 300 kW/m^2. Techniques such as CFD (Hernandez and Crespo, 1992) and wind tunnel tests (Verheij and Duijm, 1991) are used to model the heat transfer. The principal mitigation techniques investigated are insulation and water sprays.

The cooling of vessels subject to an impinging jet flame is considered in Section 16.27.

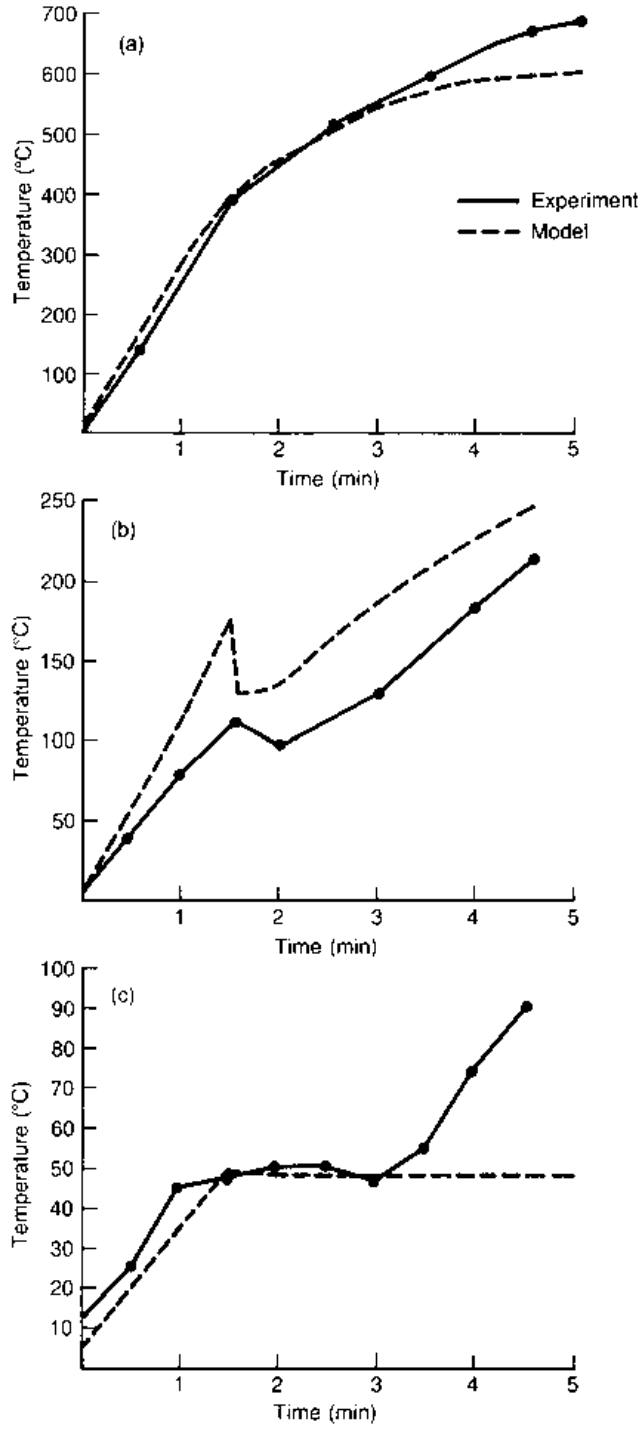


Figure 16.116 *Theoretical predictions of the temperatures in a 500 l vessel part filled with propane engulfed in fire (D.L.M. Hunt and Ramskill, 1985): (a) Outer wall (vapour space) temperature; (b) vapour temperature; (c) liquid temperature (Courtesy of the Institution of Chemical Engineers)*

16.21 Effects of Fire: Damage

Fire causes damage to property and injury to people. The statistics of fire damage and injury have been considered in Chapter 2. The modelling of fire damage is treated in this section and that of fire injury in the following one.

Broadly, fire may be treated in terms of ignition, steady- and unsteady-state combustion, and extinction, and of flame spread, both over surfaces and within buildings. An account of all these aspects is given in *An Introduction to Fire Dynamics* (Drysdale, 1985).

In this section the treatment is confined to (1) the ignition of liquids, (2) the ignition of wood and (3) the spread of flame.

16.21.1 Ignition of liquids

The susceptibility of a flammable liquid to ignition is related to the flashpoint. For high flashpoint liquids, the firepoint is also relevant. The flashpoint and firepoint of a liquid, and the methods of determination, have been discussed in Section 16.2. The firepoint is the temperature at which the liquid not just ignites but also supports a flame and it is therefore a higher temperature than the flashpoint. Essentially, the flashpoint may be obtained by experiment using closed cup or open cup methods, or by calculation as the temperature at which the vapour pressure reaches the lower flammability limit. Data on the flashpoint are available for a large number of substances. The firepoint is determined experimentally. Information on the firepoint of liquids is relatively sparse.

It was found in the work of A.F. Roberts and Quince (1973) that for a flame to be sustained on the surface of the liquid, it is necessary for the vapour concentration to be above the stoichiometric value. An apparent exception is alcohols for which the flashpoint and firepoint measured using spark ignition are the same. The maintenance of the flame on a liquid surface has been interpreted by Rasbash (1975b) in terms of the flame heat balance.

Traditionally, a liquid has been classed as highly flammable if it has a low flashpoint. Essentially the criterion value used in a particular country reflects the summer temperatures in that country. In the UK the value taken has been a temperature of less than 32°C as measured by the Abel closed cup test. For a low flashpoint liquid the hazard is that a flammable mixture will form above the liquid surface and will be ignited.

If the temperature of the liquid is high enough a vapour cloud may form. The evaporation and dispersion of such a cloud has been dealt with in Chapter 15. Vapour cloud fires have been considered in Section 16.14.

For a high flashpoint liquid to be ignited it must be heated above its firepoint. This may occur due to the play of a flame on the surface of the liquid. It has been shown by Sirignano and Glassman (1970) that if such flame impingement occurs, a surface tension effect occurs and convection currents are set up which have the effect of cooling the volume of liquid which is being heated. The liquid pool will eventually ignite but, as shown by Burgoyne and Roberts (1968a), only after the transfer of a substantial amount of heat.

Ignition of a high flashpoint liquid occurs much more readily, however, if there exists at the surface of the liquid a wick. This may take the form of a porous material such as a cloth. The liquid layer held in such a wick is too thin for the heat to dissipate and there is a rapid increase in the local temperature. The effect has been studied by Burgoyne, Roberts and Quinton (1968).

16.21.2 Ignition of solids

In the ignition of combustible solids it is usual to distinguish between (1) spontaneous, or unpiloted, ignition and (2) piloted ignition. With spontaneous ignition, also termed unpiloted ignition or auto-ignition, ignition occurs when the material has been heated up to the point where not only does it evolve vapours of volatile material but it is hot enough to ignite these vapours. With piloted ignition, by contrast, ignition of these vapours is by the pilot flame.

A further distinction may be made between the case where the pilot flame actually impinges on the surface of the solid and that where it does not. Simms (1962) refers to these situations as (1) piloted ignition (in the more restricted sense) and (2) surface ignition. This terminology is adopted here.

In this section consideration is restricted to the ignition of wood. This is the solid combustible material principally studied and it is also that of prime interest on process plants.

16.21.3 Ignition of wood

A classic study of the ignition of wood by thermal radiation is that described by Lawson and Simms (1952a,b), who subjected samples of dry wood to thermal radiation from a heated panel, with and without a pilot flame playing half an inch from the surface of the sample.

They first obtained for various kinds of wood critical values I_o of the thermal radiation intensity I below which ignition does not occur even at long exposure times. The woods used included oak, mahogany, red cedar and whitewood. For the minimum thermal radiation intensity for spontaneous ignition I_s they obtained the range of values 0.57–0.66 cal/cm^2 s with an average of about 0.62 cal/cm^2 s, and for the minimum thermal radiation intensity for piloted ignition I_p they obtained the range 0.30–0.36 cal/cm^2 s with an average of about 0.35 cal/cm^2 s. They also studied fibre insulation board, for which the critical values were 0.57 and 0.15 cal/cm^2 s for spontaneous and for piloted ignition, respectively.

For thermal radiation intensities above these threshold values they obtained the following relations. For piloted ignition*

$$(I - I_p)t_i^{\frac{2}{3}} = A \qquad [16.21.1]$$

with

$$A = 0.025 \times 10^6 (k\rho s + 68 \times 10^{-6}) \qquad [16.21.2]$$

where A is a parameter (cal^2/cm^4 (°C)^2 s), I is the thermal radiation intensity (cal/cm^2 s), I_p is the minimum thermal radiation intensity for piloted ignition (cal/cm^2 s),

* In the first edition of this book SI versions of Equations [16.21.1] and [16.21.3] given by Eisenberg, Lynch and Breeding (1975) were quoted which are incorrect, evidently due to an error in the conversion. The latter work gives incorrect dimensions for the thermal conductivity k, as do the original authors, which may be the explanation.

k is the thermal conductivity of the wood (cal/cm^2 s (°C/cm)), s is the specific heat of the wood (cal/g °C), t_i is the ignition time (s) and ρ is the density of the wood (g/cm^3).

For spontaneous ignition they obtained*

$$(I - I_s)t_i^{\frac{1}{2}} = B \qquad [16.21.3]$$

with

$$B = 0.05 \times 10^6(k\rho s + 35 \times 10^{-6}) \qquad [16.21.4]$$

where B is a parameter (cal^2/cm^4 (°C)^2 s) and I_s is the minimum thermal radiation intensity for spontaneous ignition (cal/cm^2 s).

On the assumption that surface cooling occurs, there should be an effect of the thermal inertia $k\rho s$ (cal^2/cm^4 (°C)^2 s). This is the case, in that the parameters A and B are found to be linear functions of this quantity. Values of ρ, s and k for a number of materials are given in texts on heat transfer such as that by Carslaw and Jaeger (1959).

Thus for oak the relations between thermal radiation intensity and exposure times for ignition were approximately as follows:

Ignition time, t_i (s)	*Thermal radiation intensity* (cal/cm^2 s)	
	Piloted ignition, I_p	*Spontaneous ignition*, I_s
5	1.45	
10	1.10	1.40
25	0.77	1.05
50	0.65	0.86
100	0.52	

From this work a minimum thermal radiation intensity for ignition of wood of 0.3 cal/cm^2 s (12 kW/m^2) has been used for building design. This figure was given, for example, in the Scottish Building Regulations 1971.

Further work by Simms and co-workers (Simms, 1960, 1961, 1962, 1963; Simms and Law, 1967) has shown that it is possible to determine for a given wood a minimum surface temperature for ignition.

Simms and co-workers have also developed a number of models for ignition of a thin slab and of a semi-infinite solid by radiant heat. One standard heat transfer relation applicable to a semi-infinite solid is quoted by Drysdale (1985) as follows:

$$\frac{\theta_s}{\theta_\infty} = 1 - \exp(\beta^2)\mathrm{erfc}(\beta) \qquad [16.21.5]$$

with

$$\theta_s = T_s - T_o \qquad [16.21.6]$$

$$\theta_\infty = T_\infty - T_o \qquad [16.21.7]$$

$$\beta = \frac{ht^{\frac{1}{2}}}{(k\rho c)^{\frac{1}{2}}} \qquad [16.21.8]$$

where h is a heat transfer coefficient for convection (cal/cm^2 s °C), t is the time (s), T is the surface temperature for ignition (K), T_o is the initial surface temperature (K), T_∞ is the surface temperature for ignition at infinite time (K), β is a parameter, θ_s is the surface temperature difference for ignition (°C) and θ_∞ is the surface temperature difference for ignition at infinite time (°C).

The parameter β is known as the cooling modulus. It may be written in the alternative form

$$\beta = \frac{h(\alpha_h t)^{\frac{1}{2}}}{k} \qquad [16.21.9]$$

where α_h is the thermal diffusivity (cm^2/s).

It may also be expressed in terms of the dimensionless groups

$$\beta = \mathrm{BiFo}^{\frac{1}{2}} \qquad [16.21.10]$$

with

$$\mathrm{Bi} = \left(\frac{hL}{k}\right) \qquad [16.21.11]$$

$$\mathrm{Fo} = \left(\frac{\alpha_h t}{L^2}\right) \qquad [16.21.12]$$

where L is a linear dimension, Bi is the Biot number and Fo is the Fourier number.

It has been shown by Simms (1963) that Equation 16.21.5 may be reformulated as follows. The surface temperature difference θ_∞ is related to the thermal radiation intensity I:

$$h\theta_\infty = \alpha I \qquad [16.21.13]$$

where α is the absorptivity.

Then from Equations 16.21.5 and 16.21.13

$$\theta_s = \frac{\alpha I}{h}[1 - \exp(\beta^2)\mathrm{erfc}(\beta)] \qquad [16.21.14]$$

which Simms recasts as

$$\gamma = \beta[1 - \exp(\beta^2)\mathrm{erfc}(\beta)]^{-1} \qquad [16.21.15]$$

with

$$\gamma = \frac{\alpha It}{\rho c(\alpha_h t)^{\frac{1}{2}}\theta_s} \qquad [16.21.16]$$

where γ is a parameter known as the energy modulus.

Simms obtained for various woods the relation between the energy modulus γ and the cooling modulus β shown in Figure 16.117.

Another form of the model given by Simms and Law (1967) is

$$\frac{It}{\rho c(kt)^{\frac{1}{2}}\theta_s} = \frac{\beta}{1 - \exp(\beta^2)\mathrm{erfc}(\beta)} \qquad [16.21.17]$$

These authors term the heat transfer coefficient, given above by the symbol h, the Newtonian cooling coefficient, but the two are identical. They also give values for the coefficient for various temperature differences.

The work of Simms and others has shown that for a given wood it is also possible to correlate results in terms of the minimum ignition temperatures for spontaneous ignition, pilot ignition, and surface ignition. These temperatures are discussed by Simms (1962) and Simms and Law (1967). For piloted ignition without flame contact the results obtained tend to depend on the precise positioning of the flame, though they are reproducible for a given configuration.

Further, for spontaneous ignition, woods exhibit a common minimum ignition temperature of about 545°C.

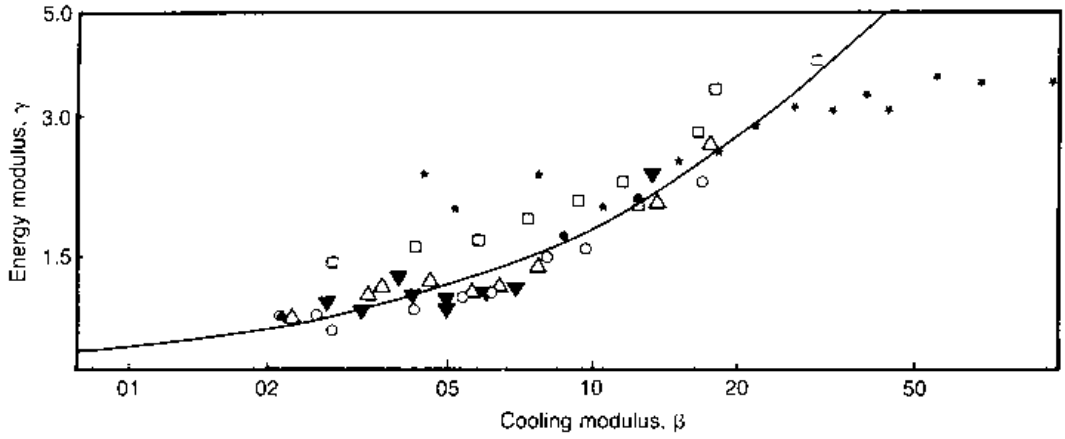


Figure 16.117 *Ignition of wood by thermal radiation: energy vs cooling modulus correlation (Simms, 1963): $\theta_s = 340°C$; $h = 33$ W/m^2 K; (*) fibre insulation board; (□)cedar; (△) freijo; (○) mahogany; (●) oak; (▼)iriko. The curve is that given by Equation 16.21.15. (Courtesy of Combustion and Flame)*

This does not apply, however, at very low rates of heating such that the volatile matter becomes exhausted without ever igniting. Likewise, there is a common minimum ignition temperature for piloted ignition of about 380°C. Taking an initial temperature of 20°C, these two minimum ignition temperatures correspond respectively to minimum ignition temperature differences θ_s of about 525°C and 360°C.

The relation between the minimum thermal radiation intensity I_o and the minimum temperature difference θ_s for ignition is

$$I_o = h\theta_s \qquad [16.21.18]$$

Thus, for example, for piloted ignition Simms and Law give a value of h of 8.6×10^{-4} cal/cm^2 s °C. Then for $\theta_s = 360°C$, $I_o = 0.31$ cal/cm^2 s.

The results described were obtained in carefully controlled experiments using dry wood samples with specified characteristics. It is known that there are effects of thermal inertia, water content, wood grain, etc., and surface absorptivity.

A material with low thermal inertia ignites more readily than one with high inertia. This effect is taken into account in the correlations given above.

The effect of water content has been studied by Simms and Law (1967). Water content influences ignition in several ways. It affects the thermal inertia of the wood through its effects on the individual properties, namely density, specific heat and thermal conductivity. In addition, it affects the overall heat transfer in two ways: heat transfer by molecular diffusion of water; and vaporization of water, which cools the hot zone, and condensation, which heats the cooler zones.

The water content of the wood increases the minimum ignition energy, the minimum thermal radiation intensity and the ignition time for both spontaneous ignition and piloted ignition without contact. But for the latter it becomes significant only at water contents of 40% or more. A water content of 60% doubles the minimum thermal intensity for piloted ignition.

The properties of the wood itself affect thermal radiation ignition. These include the cut end, the direction of the grain and any knots. One effect of grain is on thermal conductivity. Another is on the flow of volatile matter.

The absorptivity of the wood increases as charring occurs.

With regard to the thermal radiation incident on the wood, it has been shown by Kashiwagi (1979a) that there can be a significant attenuation due to the volatile matter issuing from it.

Further work on ignition of wood has been described by Wesson, Welker and Sliepcevich (1971). They use a correlation of the form

$$t_i = k_1 \rho^{n_1} (\alpha I)^{n_2} \mathrm{erf}[L/2(\alpha_h t)^{\frac{1}{2}}]^{n_3} \qquad [16.21.19]$$

where L is the thickness of the slab (cm), k_1 is a constant and n_1–n_3 are indices. For wood $\alpha_h \approx 1.5 \times 10^{-3}$ cm^2/s and for the wood samples used $L \approx 2$ cm. Using these values in Equation 16.21.19 the term $\mathrm{erf}[L/2(\alpha_h t_i)^{\frac{1}{2}}]$ is approximately unity for $t < 700$ s. From experiments on a number of woods the authors obtained values of the constant in Equation 16.21.19 to yield

$$t_i = 35\rho^{0.9}(\alpha I)^{-2.8} \qquad [16.21.20]$$

A comparison of the minimum ignition temperature for heat transfer by radiation and convection has been made by Kanury (1972a), who quotes the following approximate values:

Heat transfer mode	*Minimum ignition temperature* (°C)	
	Piloted ignition	*Spontaneous ignition*
Radiation	300–410	600
Convection	450	490

16.21.4 Flame spread

The growth of fire is frequently governed, particularly in the early stages, by flame spread over the surface of solids or liquids. Flame spread itself is considered at this point. The spread of fire through buildings is discussed in Section 16.36.

Accounts of flame spread include those given by P.H. Thomas, Simms and Wraight (1964, 1965), Burgoyne, Roberts and Quinton (1968), de Ris (1969), MacKinven, Hensel and Glassman (1970), Sirignano and Glassman (1970), Magee and McAlevy (1971), W.J. Parker (1972), Fernandez-Pello and Williams (1974), R. Friedman (1977), F.A. Williams (1977), Quintiere (1981), Suzuki and Hirano (1982), Ray and Glassman (1983), Drysdale (1985) and Ishida (1986, 1988).

The two situations considered here are flame spread across (1) a liquid surface and (2) a solid surface. In both cases the spreading flame has two effects: it serves as a source of heat and it causes pilot ignition.

In work on flame spread across a combustible liquid surface a distinction is made between a liquid which is below the fire point and one which is above it. If the liquid is below the fire point, it has first to be heated up. As described above, work by Sirignano and Glassman (1970) has demonstrated the role of surface tension effects in the circulation flows set up in the bulk liquid. Further work includes that by MacKinven, Hensel and Glassman (1970) on the effect of pool depth and width.

If the liquid is above its fire point, the flame spread is governed by flame propagation through the flammable mixture above the liquid surface. It has been found by Burgoyne and Roberts (1968a) that for a stoichiometric mixture the apparent rate of spread reaches a limiting value of some 4–5 times the fundamental burning velocity.

Work on flame spread over ground soaked with fuel has been described by Ishida (1986, 1988).

Flame spread over solid surfaces is a function of (1) the orientation and geometry of the surface, (2) the direction of propagation, (3) the thickness of the combustible material, (4) the properties of the material and (5) the environment factors.

The behaviour of a flame on a vertical surface differs from that of one on a horizontal surface. The direction of propagation also makes a radical difference. Flame spread is most rapid when propagation is upwards on a vertical surface. These differences are largely accounted for by differences in the extent to which the flame preheats the solid.

The rate of upward flame spread on a vertical surface tends to increase exponentially. It can be characterized by the time taken for the rate of spread to double, or the doubling time, as described by Alpert and Ward (1984).

For thin layers of combustible solid, the rate of flame spread has been shown by experiment and theory to be inversely proportional to the thickness of the bed. Relevant work has been described by Magee and McAlevy (1971) and Fernandez-Pello and Williams (1974).

The rate of flame spread is also a function of the thermal properties of the material. The precise relations depend on the thickness of the surface. A critical thickness exists which is

$$\tau_{cr} = (\alpha_h L/V)^{\frac{1}{2}} \qquad [16.21.21]$$

where L is the 'heating length', V is the rate of flame spread, α_{h} is the thermal diffusivity of the material and τ_{cr} is the critical thickness. The heating length is the length of solid over which the material is heated to its fire point. It can be shown that for thin surfaces $(\tau < \tau_{cr})V \propto (\rho c \tau)^{-1}$ and for thick surfaces $(\tau > \tau_{cr})V \propto (k\rho c)^{-1}$, where c is the specific heat, k is the thermal conductivity, ρ is the density of the material and τ is the thickness. Further, since the thermal conductivity k is approximately proportional to the density, in this latter case $V \propto \rho^{-2}$. Thus the rate of flame spread over the surface of a low density material can be very rapid.

The geometry of the surface also affects flame spread. There have been a number of studies of features such as width and edge effects.

Flame spread is also influenced by environmental factors, including the initial temperature of the fuel, the air velocity over the surface, the imposed thermal radiation and an oxygen enriched atmosphere.

Thermal radiation can cause a marked enhancement of the rate of flame spread, as evidenced by the work of Alvares (1975), Kashiwagi (1976), Fernandez-Pello (1977a,b), Hirano and Tazawa (1978) and Quintiere (1981) and others.

The effect of air velocity on flame spread depends on the direction of air flow. If the air flow is in the same direction as the flame spread, an increase in air velocity tends to increase the rate of spread, whilst if it is in the opposing direction the effect depends on the magnitude of the air velocity. A low air velocity tends to enhance the rate of flame spread but a high one tends to reduce it. Whichever of the two directions the air flow has, there will come a point at which a very high velocity results in flame extinction, or blow-off.

The spread of flame across surfaces has been modelled by a number of workers. F.A. Williams (1977) gives the so-called 'fundamental equation of fire spread'

$$\rho V \Delta H = \dot{q} \qquad [16.21.22]$$

where ΔH is the enthalpy change per unit mass in raising the material to its firepoint, $\dot{q}$ is the rate of heat transfer across the surface, V is the rate of flame spread and ρ is the density of the fuel.

The rather different problem of flame spread through open fuel beds has been studied by P.H. Thomas, Simms and Wraight (1964, 1965), who conducted a classic set of experiments on wooden cribs. Their results have been applied by other workers to a variety of fire situations.

In practical cases some factors which are of particular importance in determining flame spread over a solid surface are the thickness and composition of the surface, the imposed thermal radiation and the air movement over the surface.

16.21.5 Thermal radiation limits

Thermal radiation limits are quoted in a number of codes and standards and in numerous papers. Many limits are given for the purposes of plant design and layout. Some are relevant to hazard assessment. Generally, such sets of limits include both limits related to damage and others related to injury. It is convenient, therefore, to defer consideration of such limits to the next section.

16.22 Effects of Fire: Injury

There is a requirement in hazard assessment for relationships which permit heat radiation intensity to be translated into the equivalent burn injury. Correlations for both fatal and non-fatal burn injury have been derived in the vulnerability model by Eisenberg, Lynch and Breeding (1975). A detailed review and additional information have been given by Hymes (1983 SRD R275). Further correlations are given in the *Green Book* (CPD, 1992b).

16.22.1 Sources of thermal radiation

The effect of thermal radiation on man depends very much on the source of radiation and it is therefore necessary to specify this. One source of thermal radiation which is of long-standing interest is a flare and some of the earliest thermal radiation limits relate to flares.

Another source of thermal radiation which has received increasing attention is a fireball, typically as part of a BLEVE. A fireball is well defined relative to most other types of fire to which people may be exposed and it is one of the fire hazards most likely to give rise to a large number of serious injuries.

16.22.2 Experimental studies

Experimental work on injury from thermal radiation has been done on humans and on animals. The use of human subjects is limited to the lower levels of pain and injury.

Henriques (1947) carried out experiments in reddening and blistering in man exposed to thermal radiation. Buettner (1951b) performed experimental work on man in which skin temperature and pain threshold were measured. Experiments on man were also conducted by Stoll and Greene (1959) to investigate skin temperature and thresholds of pain and blistering.

Experimental work on rats exposed to thermal radiation by NML, Brooklyn, and on rats exposed to direct flame contact by NADC, Johnsville, quoted by Stoll and Chianta (1971), provides a basis for comparing burn injury by these two modes.

Hinshaw (1957) at the University of Rochester investigated the thermal radiation intensities required to produce second and third degree burns in pigs. Experiments on swine burn have also been performed by Hardee and Lee (1977/78).

Tests on the response of fabrics to thermal radiation have been done by Wulff and co-workers (Wulff, 1973; Wulff *et al.*, 1973; Wulff and Durbetaki, 1974), and work on heat transfer from burning clothing to the wearer has been done by Williams *et al.* (n.d.) at MIT and by Arnold *et al.* (1973) at the Gillette Research Institute.

16.22.3 Skin properties

Human skin consists of two layers, the epidermis and the dermis. It ranges in thickness from some 5 mm on the back to some 0.5 mm on the eyelids. The area of skin on the average man is some 1.8 m^2. The distribution of skin surface area is considered in Section 16.22.10.

16.22.4 Pathology of burns

Accounts of burns and burn treatment are given in *Burns and Their Treatment* (I.K. Muir and Barclay, 1974), *Burns: a Team Approach* (Artz, Moncrief and Pruit, 1979), *Clinical Burn Therapy* (Hummel, 1982), *Physiological Responses to Burn Injury* (J.W.L. Davies), *Burn Mortality* (W. Clark and Fromm, 1987), *Plastic Surgery* (Goldin, 1987) and *Plastic Surgery* (McCarthy, 1990). Treatments of burn injuries of particular relevance here are those by Glasstone (1962) and Hymes (1983 SRD R275).

The effects of incident heat radiation are, in order of increasing severity:

Burn type	*Criterion*
First degree	Persistent redness
Second degree:	
Moderate	Some blistering
Deep	Full blistering
Third degree	Charring

A first degree burn involves the epidermis. There is reddening but no blistering. A second degree burn may be superficial or deep. The former affects the epidermis and part of the dermis and involves some blistering, but with damage to the surface layers only. The latter penetrates further into the dermis and damages it more severely. A third degree burn destroys both the epidermis and the dermis.

The terms second and third degree burn have largely given way to characterization in terms of the depth of burn, reference being made to full depth and other burns.

16.22.5 Skin temperature

Burn injury correlates closely with skin temperature. Pain is experienced at a temperature of 44°C and above this temperature injury occurs.

Relations for the unsteady-state temperature profile of the skin suddenly exposed to a source of heat radiation have been given by Buettner (1951a) and by Stoll and Chianta (1971). The simplest of these is the equation given by Buettner for a non-penetrating constant source of thermal radiation:

$$T_s - T_o = \frac{2Qt^{\frac{1}{2}}}{(\pi k \rho c)^{\frac{1}{2}}} \qquad [16.22.1]$$

where for the skin c is the specific heat, k is the thermal conductivity, Q is the net heat absorbed, t is the time, T_o is the initial temperature throughout, T_s is the surface temperature and ρ is the density.

The thermal response is governed by the thermal inertia ($k\rho c$). Measurements of the thermal inertia were made by Stoll and Greene (1959), who found that it varied strongly with the thermal radiation intensity.

Stoll and co-workers (Stoll and Greene, 1959; Stoll and Chianta, 1971) have studied the temperature at the basal layer of skin, which is about 80 μm (0.08 mm) below the surface. They found that damage occurs at temperatures above 44°C.

The temperature profile of skin at 80 μm subjected to thermal radiation sufficient to cause blistering given by these workers is shown in Figure 16.118(a). They give a model for the degree of tissue damage W due to heat radiation. Part of the damage occurs during the cooling period after the heat source is removed.

The rate of injury above 44°C increases very rapidly indeed with temperature. The relation given by Stoll and Chianta is shown in Figure 16.118(b). There is an approximate trebling of the rate of injury for each 1°C temperature rise. Thus the injury rate at 50°C is some 100 times that at 44–45°C.

Stoll and Chianta describe work on burns in rats. The responses of rats to thermal radiation and to flame contact have been studied by NML, Brooklyn, and by NADC, Johnsville, respectively. Figure 16.118(c) gives a comparison of the two sets of results which shows that the responses are virtually identical. These results indicate that the dose–response relation is similar for thermal radiation and for flame contact. The results are usually regarded as applicable to man also.

16.22.6 Injury factor

Injury due to exposure to a short but strong pulse of thermal radiation may be correlated in several ways. The most convenient is to take the injury factor as the thermal dose which is the product of the thermal radiation intensity and time. The level of thermal radiation for a particular effect is often correlated in terms of the thermal dose.

It is found, however, that this somewhat understates the effect of very high intensities of thermal radiation and that better correlation is obtained if these are more highly weighted. The empirical correlation for the injury factor which best fits the data is

$$tI^n = \text{Constant} \qquad [16.22.2]$$

where I is the intensity of thermal radiation (W/m^2), t is the time (s) and n is an index.

As described below, Equation 16.22.2 has been given by Eisenberg, Lynch and Breeding (1975) for the correlation of data on burn fatalities with a value of the index $n = 4/3 = 1.33$. For non-fatal burn injuries these authors use the slightly different exponent $n = 1.15$. It has been proposed by Hymes that the data for fatal and non-fatal injury are adequately correlated using a value of $n = 1.33$ for both.

The term $tI^{\frac{4}{3}}$ is referred to here as the thermal load L to distinguish it from the thermal dose $D = tI$. It is conventional to express the thermal radiation intensity in kW/m^2 but to use in probit equations an intensity expressed in W/m^2. Since this latter practice gives rise to thermal loads which are large numbers, it is convenient to define also an alternative thermal load L'. These quantities are thus defined as follows:

$$D = tI \qquad [16.22.3]$$

$$L = tI^{\frac{4}{3}} \qquad [16.22.4]$$

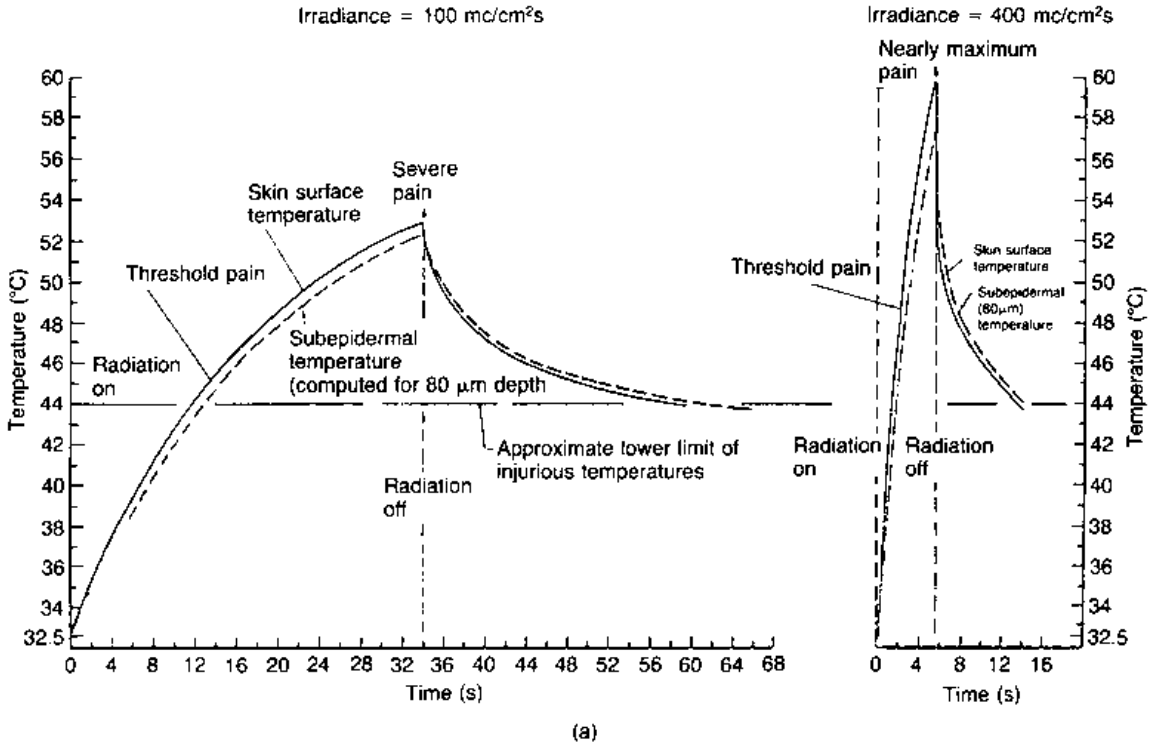
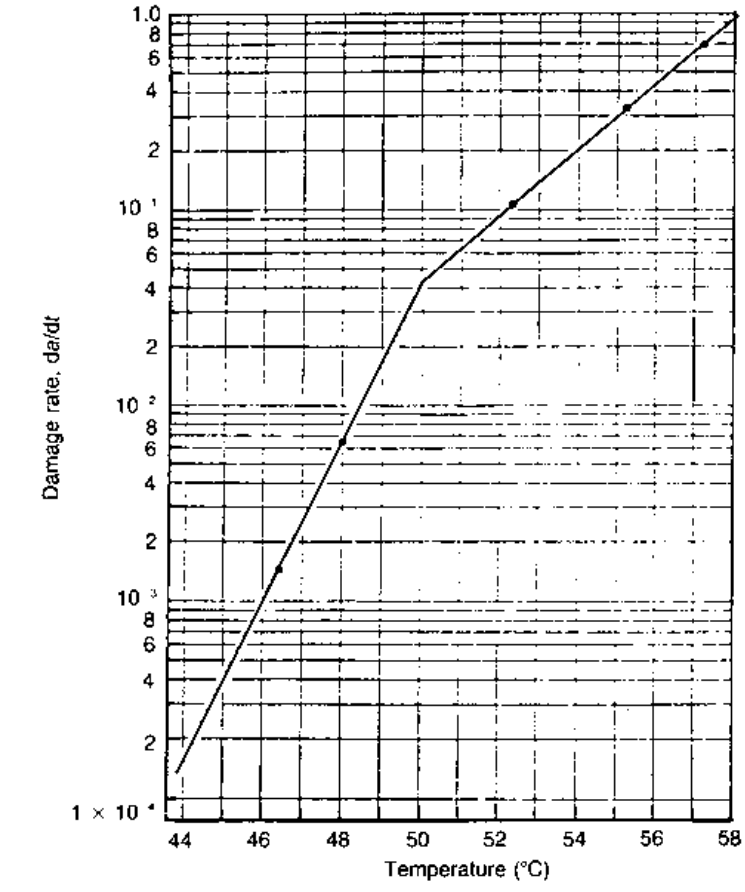
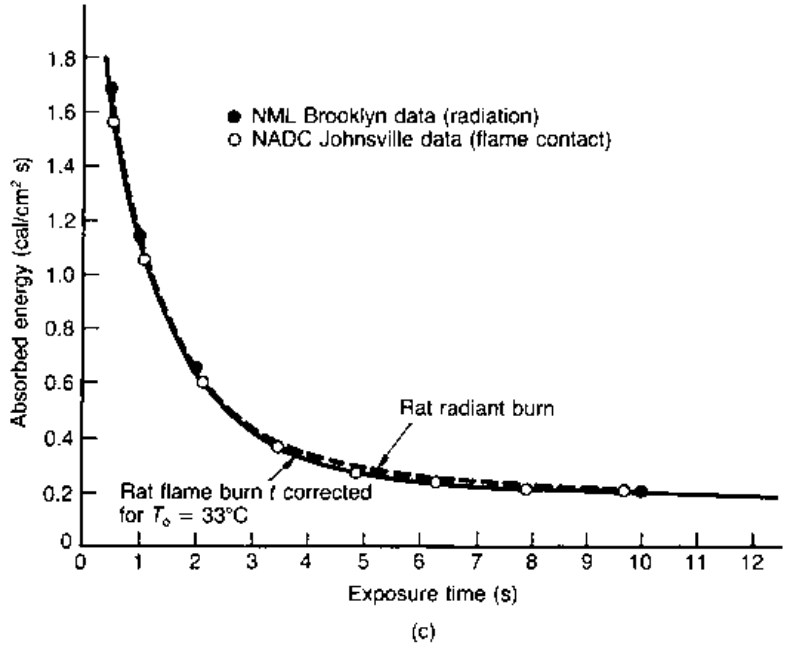


Figure 16.118 *Effect of heat on skin (Stoll and Chianta, 1971): (a) heating and cooling of skin exposed to heat radiation.*



(b)



(c)

Figure 16.118 *Continued (b) rate of damage to skin exposed to heat radiation; and (c) burn injury to rats exposed to heat radiation and to flame contact (Courtesy of the New York Academy of Sciences)*

where D is the thermal dose (kJ/m^2), I is the thermal radiation intensity (kW/m^2), L is the thermal load (s (kW/m^2)$^{\frac{4}{3}}$) and t is the exposure time (s). Further

$$L' = tI^{\frac{4}{3}}/10^4 \qquad [16.22.5]$$

where I is the thermal radiation intensity (W/m^2) and L' is the thermal load ((s (W/m^2)$^{\frac{4}{3}}$)/10^4).

16.22.7 Pain and blister thresholds

A number of workers have correlated thresholds of pain and blistering. Table 16.75 shows some limits for pain and injury given in the literature, in terms of thermal radiation intensity in Section A and of thermal dose in Section B.

Table 16.76, Section A, shows the results obtained for the time to the threshold of pain in man by Buettner (1961b) and by Stoll and Green (1959). Figure 16.119(a) (Mudan, 1984c) is a plot of data reported by these and other workers.

The threshold of pain may also be expressed in terms of the thermal load. Values given by Hymes based on the work of Stoll and Greene are shown in Table 16.76, Section C. Hymes gives as the approximate threshold of pain a value of 92 s (W/m^2)$^{\frac{4}{3}}$/10^4.

Results for the time to the threshold of blistering in man by Stoll and Greene are shown in Table 16.76, Section B, whilst a plot by Mudan of these and other data is given in Figure 16.119(b).

16.22.8 Second and third degree burns

Several workers have investigated the degree of exposure of pigs to levels of thermal radiation which cause second and third degree burns. In work by Hinshaw (1957) at the University of Rochester, pigs were subjected to thermal radiation exposures of 210, 420 and 670 kJ/m^2 for periods of 0.5, 1, 3, 5, 10 and 30 s.

At high thermal radiation intensities the heat is sufficient to vaporize the tissue fluids, an effect known as ablation. The burn injury occurring in these circumstances is termed a 'steam bleb'. Histological examination in these experiments showed that the thermal radiation was sufficiently intense in some tests to cause steam 'bleb' formation and mitigation of the tissue damage.

The data have been analysed by Hymes who has derived the results given in Table 16.77 correlated in

Table 16.75 *Some limits for pain and injury from thermal radiation*

A Thermal radiation intensity

Thermal radiation intensity (kW/m^2)		*Reference*
1.5	Threshold of pain	Atallah and Allan (1971)
2.1	Level at which pain is felt after 1 minute	
1	Level just tolerable to a clothed man	HSE (1978b)
8	Level which causes death within minutes	
4.7	Threshold of pain. Average time to experience pain, 14.5 s	Crocker and Napier (1986)

B Thermal dose

Thermal dose (kJ/m^2)		*Reference*[a]
40	Second degree burns	Williamson and Mann (1981)[a]
125	Third degree burns	
65	Threshold of pain	Rijnmond Public Authority
125	First degree burns	(1982)
250	Second degree burns	
375	Third degree burns	
*c.*100	Threshold of blistering	Crossthwaite (1984)[a]
200	Blistering	
700	50% fatality	
65	Threshold of pain, no reddening or blistering of skin	BS 5908: 1990
125	First degree burns	
200	Onset of serious injury	
250	Second degree burns	
375	Third degree burns	

[a] For thermal radiation from a fireball.

Table 16.76 Times to pain and blister thresholds

A Time to threshold of pain: thermal radiation intensity

Authors	*Thermal radiation intensity* (kW/m^2)	*Time* (s)
Stoll and Greene (1959)[a]	4.2	13.5
	5.2	10.1
	6.3	7.8
	8.4	5.5
	12.6	2.9
	16.8	2.2
Buettner (1951b)[b]	3.7	20
	6.2	10
	9.7	5
	18	2
API RP 521: 1990	1.74	60
	2.33	40
	2.90	30
	4.73	16
	6.94	9
	9.46	6
	11.67	4
	19.87	2

B Time to threshold of blistering: thermal radiation intensity

Authors	*Thermal radiation intensity* (kW/m^2)	*Time* (s)
Stoll and Greene (1959)	4.2	33.8
	6.3	20.8
	8.4	13.4
12.6	7.8	
16.8	5.6	

C Time to threshold of pain: thermal load

Authors	*Thermal load,* $tI^{\frac{4}{3}}$ ($s\,(W/m^2)^{\frac{4}{3}}/10^4$)	*Time* (s)
Hymes (1983 SRD R275)	86	13.0
	88	10.0
	90	8.0
	91	5.5
	103	3.0

[a] Time to threshold of pain.
[b] Time to unbearable pain.

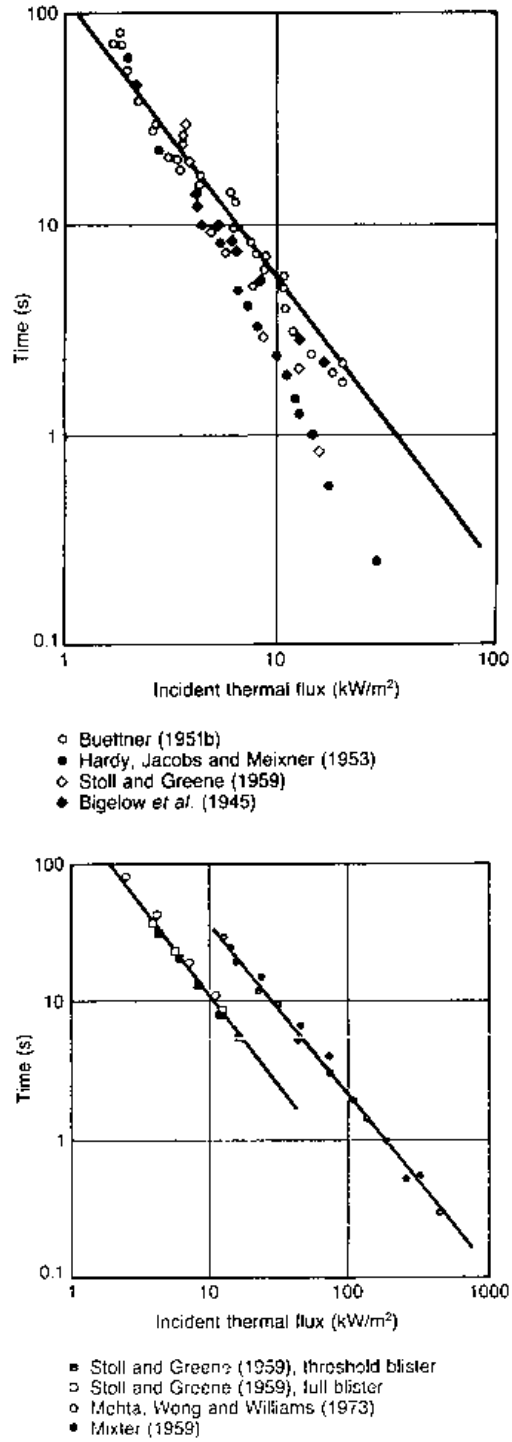


Figure 16.119 *Time to threshold effects of heat radiation (Mudan, 1984c): (a) threshold of pain; and (b) threshold of blistering (Courtesy of* Progress in Energy and Combustion Science*)*

Table 16.77 *Second and third degree burn injury to pigs exposed to thermal radiation (after Hymes, 1983 SRD R275) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Thermal dose (kJ/m^2)	*Time* (s)	*Thermal load* ($s\,(W/m^2)^{\frac{4}{3}}/10^4$)	*Dermal damage* (mm)	*Steam bleb*
210	0.5	1570	0.17	No
	1	1240	0.16	No
	3	860	None	No
	5	730	None	No
	30	400	None	No
420	0.3	4680	0.49	Yes
	3	2170	0.72	No
	10	1450	0.45	No
670	0.5	7385	0.9	Yes
	1	5860	1.1	Yes
	3	4065	1.4	Sometimes
	5	3430	1.6	No
	10	2720	1.6	No
	30	1890	1.1	No

terms of the heat injury factor. From these data Hymes estimates the threshold for steam bleb formation as a thermal load of some 4000–4500 $s\,(W/m^2)^{\frac{4}{3}}/10^4$. This is a very high level of thermal radiation which, according to the relations for fatality given below, would be lethal in some 90% of cases. It is therefore thermal radiation intensity below the level of steam bleb formation which is of prime interest.

The depth of skin burn in Hinshaw's experiments at thermal radiation intensities below those which cause steam bleb has been correlated by Hymes, as shown in Figure 16.120(a). He takes the burn depths for the threshold of second degree burns and the onset of third degree burns as 0.1 and 2 mm, respectively. The corresponding thermal loads are approximately 1200 and 2600 $s\,(W/m^2)^{\frac{4}{3}}/10^4$, respectively.

Swine burn experiments have also been done by Hardee and Lee (1977/78), who have derived from their results considerably lower values for the levels of heat radiation intensity for given degrees of injury. According to Hymes, the reinterpretation of this work does not support these lower values.

As described above, work has been done at MIT and at the Gillette Research Institute on the heat transferred from burning clothing to the wearer.

Figure 16.120(b) shows the relation between depth of skin burn and thermal load from these sources as given by Hymes.

Another source of information on second and third degree burns is data on burn victims from the nuclear weapons dropped on Japan, which are given by Glasstone (1962).

16.22.9 Human response to fire events

Human response to a fire event depends on (1) the nature of the event and (2) the awareness of the person.

The event primarily considered in relation to burn injury is a fireball. Another sudden event may be a rapid growth in the size of a flare. Other types of event such as a pool fire are generally considered to occur more gradually and to allow more time for escape, though this may not always be so. It is the fireball hazard which is primarily considered by Hymes and Marshall, and also here.

Accounts of burn injury such as those by Hymes and in the *Green Book* quote a human response time of 5 seconds. The application of this reaction time to a fireball scenario is that the person faces the fireball for 5 seconds and then turns his back and seeks to escape.

In an analysis of human exposure to a BLEVE, in the context of a discussion of the disaster at San Carlos, Hymes considers two situations. In Situation 1 with the lift-off time less than the reaction time, the first phase involves frontal exposure for the 5 second reaction time. The person then turns his back and seeks to escape. During this escape the fireball passes through three further phases: further growth at ground level, shrinkage just prior to lift-off, and rise. In Situation 2, the lift-off time equals the reaction time, so that there is no phase of further growth at ground level; otherwise the scenario is similar, with the period of frontal exposure again being 5 seconds.

In practice, human behaviour tends to be more complex. Hymes gives an account of the BLEVE at the Lowell Gas Company at Tewkesbury, Massachusetts, in 1972. One comment quoted contains two relevant points. The fire fighters seem to have had 'momentary warning' of the impending BLEVE. Since the front of their clothing was not burned but the back was, they appear to have turned their backs very promptly, but since their faces were burned, it is believed that they tended to look round to see what was happening.

16.22.10 Protection by clothing

The degree of protection offered by clothing depends on the fraction of the body which is so protected. Data on the fraction of the body area represented by the different parts of the body are given in the *Green Book*. An extract

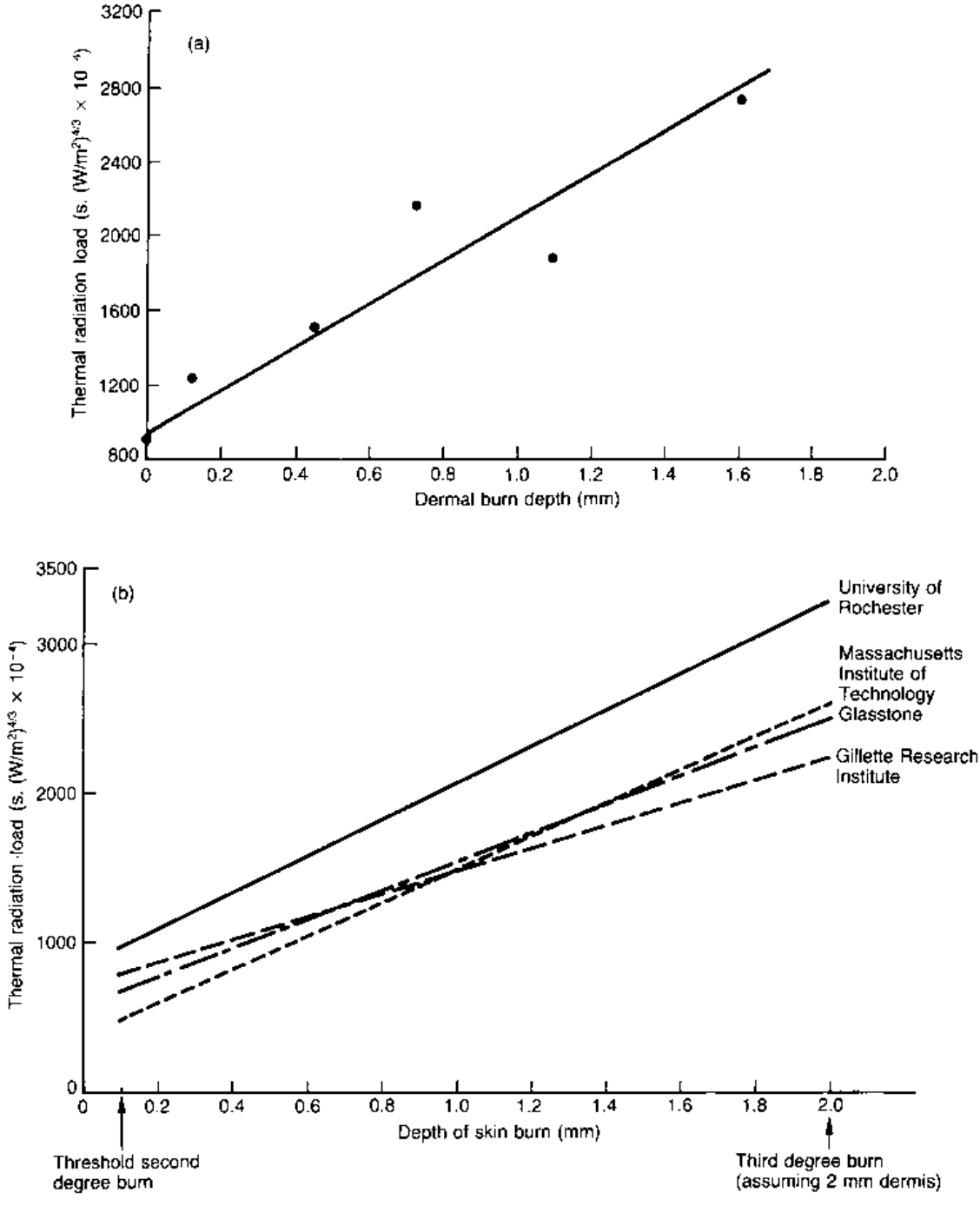


Figure 16.120 *Depth of skin burn due to heat radiation (Hymes, 1983 SRD R275): (a) sub-'steam bleb' burns in pigs obtained at University of Rochester by Hinshaw; and (b) comparison with results of other workers (Courtesy of the UKAEA Safety and Reliability Directorate)*

from this tabulation, giving the fraction of body area (%) for the parts of the body most likely to be exposed, is as follows:

Fraction of body area (%)						
Part of body	*Age group (years)*					
	1	1–4	5–9	10–14	15	*Adult*
Head	19	17	13	11	9	7
Neck	2	2	2	2	2	2
Hands (each)	2.5	2.5	2.5	2.5	2.5	2.5
Lower arms (each)	3	3	3	3	3	3
Upper arms (each)	4	4	4	4	4	4
Lower legs (each)	5	5	5.5	6	6.5	7
Upper legs (each)	5.5	6.5	8	8.5	9	9.5

The *Green Book* takes for the Dutch population a maximum value of the body surface exposed of 20% in normal conditions.

From the above data the following estimates of the fractions of body area (%) exposed for an adult may be obtained:

	Fraction of body area (%)		
	Front	*Back*	*Total*
Head	4	3	7
Neck	1	1	2
Hands	2.5	2.5	5
Lower arms	3	3	6
Total	10.5	9.5	20

If the thermal radiation is so intense as to ignite the clothing, a different situation pertains. This is considered in Section 16.22.13. A detailed discussion of the protection afforded by clothing is given by Hymes.

16.22.11 Protection by buildings

The degree of protection afforded by a building to a person within it depends on the location of that person. In many cases this will be such that the building affords complete protection. Persons in buildings are liable to be exposed, however, to thermal radiation through glass windows. A person aware of an event outside may well move to view it through a window.

Figure 16.121 from Hymes shows the transmissivity of window glass for thermal radiation from sources up to 1200°C.

16.22.12 Effective radiation intensity

In estimating burn injury it is important to utilize an appropriate value of the thermal radiation. The effective intensity is determined by the atmospheric transmissivity and the geometry of the body as presented to the radiation source. The attenuation due to the atmosphere has been discussed in Section 16.13 and is not considered further here.

The importance of the geometry of the body has been emphasized by V.C. Marshall (1987). There is a tendency in hazard assessments to treat the whole of the exposed area of the body as subject to the radiation nominally incident at the particular point. If the body is treated as a thin object, the ratio of the surface area to the projected is approximately 2. If it is treated as a long cylinder, the ratio is π. For a sphere the ratio is 4. The three-dimensional nature of the body is therefore significant. The thermal radiation incident on the exposed area is appreciably less than that calculated as falling on the projected area.

A related aspect is that with a three-dimensional body the angle of incidence of the radiation varies from 90° to close to zero. Typically, the view factor used takes

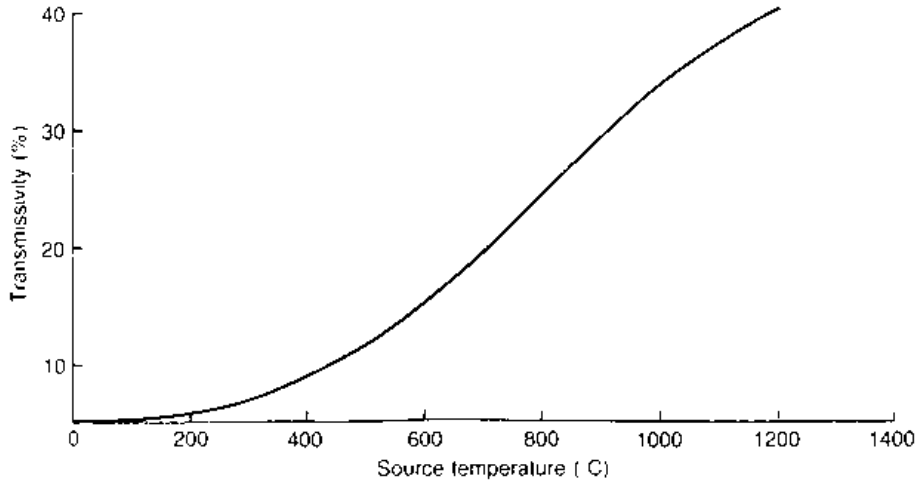


Figure 16.121 *Transmissivity of ordinary window glass for heat radiation (Hymes, 1983 SRD R275) (Courtesy of the UKAEA Safety and Reliability Directorate)*

account of the angle of incidence in two dimensions, but not three.

16.22.13 Ignition of clothing

The protection afforded by clothing is limited by the fact that at thermal radiation intensities within the range of interest here it is prone to ignite. A distinction needs to be made between everyday clothing and fire fighters' suits; the latter are naturally designed to resist ignition. It is primarily everyday clothing which is considered here.

For clothing subject to thermal radiation, there is also a distinction to be made between spontaneous and piloted ignition. A similar distinction is made for ignition of wood by thermal radiation, as described in the previous section. Whilst spontaneous ignition may be regarded as the base case, Hymes suggests that in certain scenarios, notably a BLEVE, the probability of piloted ignition, for example by burning paper or leaves, is quite high.

As already stated, work on ignition of fabrics has been carried out by Wulff and co-workers. From this work Hymes has given relations for the determination of the times to unpiloted and to piloted ignition together with tables of parameters for common fabrics.

For spontaneous ignition times are correlated by Hymes using the relation

$$tI^n = \text{Constant} \qquad [16.22.6]$$

where I is the thermal radiation intensity (W/m^2), t is the time (s) and n is an index. The values quoted for n lie in the range 1.16–3.22.

Using this equation, Hymes gives for one fabric subject to a thermal radiation intensity of $198\,kW/m^2$ the following estimate of the induction time for ignition:

$$t = \frac{2.87 \times 10^{18}}{(198\,000)^{3.44}} = 1.7\,s$$

For piloted ignition the approach is slightly different. In this case the time is taken as that required to heat the fabric from its initial temperature to its piloted ignition temperature:

$$t_p = \frac{SC(T_p - T_o)}{aW} \qquad [16.22.7]$$

where a is the absorptivity of the fabric, C its specific heat ($J/g\,^\circ C$) and S its density (g/cm^2), t_p is the time to piloted ignition (s), T_o is the initial temperature of the fabric (°C), T_p is the piloted ignition temperature (°C) and W is the incident heat radiation (W/cm^2). It should be noted that the density is defined in terms of the mass per unit thickness. Values of the piloted ignition temperature and other properties of the fabric are tabulated by Hymes.

He gives as an example a fabric subjected to a thermal radiation intensity of $198\,kW/m^2$, hence $W = 19.8\,W/cm^2$, with the properties $a = 0.19$, $C = 1.35\,J/g\,^\circ C$; $S = 0.024\,g/cm^2$, and at conditions $T_o = 14^\circ C$ and $T_p = 334^\circ C$, yielding $t_p = 2.75\,s$.

Hymes states that for thermal radiation intensities greater than $75\,kW/m^2$ most clothing will undergo spontaneous ignition within about 5 s. Under conditions such as a BLEVE, piloted ignition is probable and the time to ignition will tend to be even shorter.

The *Green Book* refers to the work of Hymes and proposes for the ignition of clothing the following threshold relation

$$tI^2 = D_s \qquad [16.22.8]$$

where D_s is the clothing ignition load ($s\,(kW/m^2)^2$), I is the thermal radiation intensity (kW/m^2) and t is the time (s). It states that the value of D_s lies approximately in the range 2.5×10^4 and $4.5 \times 10^4\,s\,(kW/m^2)^2$.

Ignition of clothing has two main effects. One is that it distracts the wearer. He may well stop running and try to douse the flames, with effects not only on the speed of escape but also on the orientation of the body.

The other effect is to cause injury from burning clothing. For the heat released by the burning of clothing, Hymes quotes the following figures for typical clothing such as cotton. The heat of combustion lies in the range 5–20 kJ/g which translates to 1–4 J/mm^2 of fabric. When the clothing burns there is transfer of some 15–50% of the heat of combustion. The thermal dose received would then be of the order of $105–356\,kJ/m^2$. He also refers to the medical adage that 'one square centimetre of burnt fabric equals one square centimetre of burnt skin'.

Mortality from burning clothing is discussed in the next subsection.

16.22.14 Mortality from burns

Information on the mortality in persons admitted to hospital with burn injuries has been given in a series of papers spanning some 40 years by Bull, Lawrence and co-workers, the first being that of J.P. Bull and Squire (1949) and the most recent that of J.C. Lawrence (1991), the intermediate publications being those of J.P. Bull and Fisher (1954) and J.P. Bull (1971).

Table 16.78 from J.C. Lawrence (1991) shows the mortality among persons admitted with burns or scalds as a function of fraction of the body exposed and of age group. The total number of cases in the 7-year survey period was 3044.

Analysis of the data given by Lawrence indicates the following breakdown of causes of burn injury in the admissions treated:

	Proportion (%)	
	Admissions	*Fatalities*
Building fires	3	16
Flammable liquids	10	21
Space heating	8	19
Electrical fire/flashover	~ 20	
Chemicals	~ 20	
Explosions, molten metal	~ 25	
Hot objects, chemicals and molten fats	14	Low
Other		
Total	100	

The proportion of burn victims who die without ever being admitted is not stated, but it is probably small. An appreciable fraction of such cases is likely to be victims of building fires who have died from both smoke and burns. Table 16.78 takes account of vulnerable groups,

Table 16.78 *Mortality in cases admitted to hospital with burn and scald injuries as a function of body area exposed and age group (J.C. Lawrence, 1991) (Courtesy of the Fire Safety Journal)*

Body area burned (%)	*Age* (years)																	
	0–4	*5–9*	*10–14*	*15–19*	*20–24*	*25–29*	*30–34*	*35–39*	*40–44*	*45–49*	*50–54*	*55–59*	*60–64*	*65–69*	*70–74*	*75–79*	*80–84*	*85+*
93+	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
88–92	0.9	0.9	0.9	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
83–87	0.8	0.8	0.9	0.9	0.9	1	1	1	1	1	1	1	1	1	1	1	1	1
78–82	0.8	0.8	0.8	0.8	0.9	0.9	0.9	1	1	1	1	1	1	1	1	1	1	1
73–77	0.7	0.7	0.7	0.8	0.8	0.8	0.9	0.9	0.9	1	1	1	1	1	1	1	1	1
68–72	0.6	0.6	0.6	0.7	0.7	0.8	0.8	0.8	0.9	0.9	1	1	1	1	1	1	1	1
63–67	0.5	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	1	1	1	1	1	1	1
58–62	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.9	0.9	1	1	1	1	1	1
53–57	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.8	0.9	1	1	1	1	1	1
48–52	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.7	0.8	0.9	1	1	1	1	1
43–47	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.7	0.9	1	1	1	1	1
38–42	0	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.6	0.8	0.9	1	1	1	1
33–37	0	0	0	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.5	0.7	0.9	1	1	1	1
28–32	0	0	0	0	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.5	0.8	0.9	1	1	1
23–27	0	0	0	0	0	0	0	0.1	0.1	0.1	0.2	0.2	0.4	0.6	0.8	0.9	0.9	1
18–22	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	0.3	0.5	0.7	0.8	0.8	0.9
13–17	0	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.3	0.5	0.6	0.6	0.7
8–12	0	0	0	0	0	0	0	0	0	0	0	0	0.1	0.2	0.3	0.4	0.4	0.4
3–7	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	0.2	0.2
0–2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1	0.1

the elderly being particularly at risk from this mode of injury.

Burn injury is an area where there have been great improvements in medical treatment over the years. One aspect of this mentioned by Craven (1976) is the improvement in survival rates since 1965 due to silver nitrate prophylaxis.

Lawrence states that over the 40-year period up to 1991 deaths attributable to burns and scalds have halved. Since the situation reported by Bull in 1971, mortality has decreased by 19%. The data given in the table therefore take account of the effects of modern medical treatment.

Work is available by Arnold *et al.* (1973) on the degree of incapacitation as a function of the fraction of body area burned. Graphs from this work are given by Hymes.

With regard to fatal injury from ignited clothing, in a survey of five American hospitals by Schlapowsky (1967) of 179 people admitted to hospital suffering from burns from clothing, almost 40% had second degree burns or worse, requiring extensive surgery and skin grafts; 16% had third degree burns.

In his survey, Lawrence states that there were 248 cases of ignition of ordinary clothing, excluding those involving flammable liquids, of whom 46 died, giving a mortality of 18.5%.

16.22.15 Eisenberg, Lynch and Breeding models

An early set of relations for thermal injury were those given in the vulnerability model by Eisenberg, Lynch and Breeding (1975). For fatal injury, these authors utilize an adaptation of data given by C.S. White (1971) for the thermal injuries caused by nuclear weapons dropped on Japan. The data of the latter author for thermal radiation are based on the weapon yield. Using a formula given by Glasstone (1962) for the relationship between weapon yield and pulse duration, Eisenberg, Lynch and Breeding convert the original data to thermal radiation intensities over a defined pulse. The figures obtained are summarized in Section A of Table 16.79.

From analysis of these data the authors obtain the data shown in the first four columns of Section B of Table 16.79. Further analysis indicated that the form of the causative factor, in this case a thermal load, should be the $I^{\frac{4}{3}}$, which is confirmed by the relative constancy of

Table 16.79 *Estimated relations between thermal radiation intensity and burn injury (after Eisenberg, Lynch and Breeding, 1975)*

A Nuclear weapons: effects and thermal injury

Thermal radiation intensity (cal/cm²s)			
Weapon yield	20 kt	1 Mt	20 Mt
Pulse duration	1.43	10.1	45.2
Thermal injury			
First degree burn	1.75	0.297	0.0886
Second degree burn	3.14	0.643	0.221
Lightly clothed (summer)			
Few, if any, injuries	1.75	0.297	0.0886
Significant injury threshold	2.80	0.594	0.210
Lethality			
Threshold	3.50	0.792	0.243
Near 50%	6.30	1.385	0.442
Near 100%	14.0	3.07	0.952

B Thermal radiation intensity and mortality

Mortality (%)	*Duration* (s)	*Thermal radiation intensity*		*Thermal load,* $tI^{\frac{4}{3}}$
		($cal/cm^2\,s$)	(W/m^2)	($s\,(W/m^2)^{\frac{4}{3}}$)
1	1.43	3.50	146×10^3	1099×10^4
1	10.1	0.792	33.1×10^3	1073×10^4
1	45.2	0.243	10.2×10^3	1000×10^4
50	1.43	6.30	263.6×10^3	2471×10^4
50	10.1	1.385	57.95×10^3	2264×10^4
50	45.2	0.442	18.5×10^3	2210×10^4
99	1.43	14.0	586×10^3	7008×10^4
99	10.1	3.07	128×10^3	6546×10^4
99	45.2	0.952	39.8×10^3	6149×10^4

the three sets of figures for 1, 50 and 99% mortality in the last column of Section B.

The probit equation derived by these authors is then

$$Y = -14.9 + 2.56 \ln(tI^{\frac{4}{3}} \times 10^{-4}) \qquad [16.22.9]$$

where I is the thermal radiation intensity (W/m^2), t is the time of exposure (s) and Y is the probit.

Since Equation 16.22.9 is based on burn injuries to people going about their normal affairs, it applies to persons who are clothed. The same equation is applied by these authors to burn injury both from flash fires and pool fires. In their model system the values of thermal radiation intensity and of time are for flash fires the effective values and for pool fires the actual values.

Eisenberg, Lynch and Breeding also give the following relation for the threshold of burns, or first degree burns, obtained from the values in Table 16.79:

$$tI^{1.15} = 550 \times 10^3 \qquad [16.22.10]$$

16.22.16 Hymes' models

The review of burn injury given by Hymes, which has already been extensively quoted, does not include any new model as such. For fatal injury Hymes utilizes Equation 16.22.9 of Eisenberg, Lynch and Breeding. He also gives a number of thermal injury effects which are summarized in Table 16.80.

The work of Hymes covers most of the relevant aspects of burn injury, including clothing ignition, thresholds of pain and blistering, and burn fatalities.

Some of the heat radiation limits and dose–response relations given by Hymes are shown in Figure 16.122, and others are given in the tables in Section 16.22.20.

16.22.17 *Green Book models*

A set of relations for thermal injury are given in the *Green Book*. For fatal injury, use is made of an adaptation of Equation 16.22.9 by Eisenberg, Lynch and Breeding. The modification is based on the fact that thermal radiation from nuclear weapons is in the UV range, whereas that from hydrocarbons is in the IR range.

Two relations are given, one for persons unprotected by clothing and one for those so protected. These are:

$$Y = -36.38 + 2.65 \ln(tI^{\frac{4}{3}}) \qquad \text{Unprotected} \qquad [16.22.11]$$

$$Y = -37.23 + 2.56 \ln(tI^{\frac{4}{3}}) \qquad \text{Protected} \qquad [16.22.12]$$

where I is the thermal radiation intensity (W/m^2) and t is the time of exposure (s).

Table 16.80 *Some limits and dose–response relations for heat radiation (after Hymes, 1983 SRD R275) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Thermal load $(s\,(W/m^2)^{\frac{4}{3}}/10^4)$	*Effect*
210–700[a]	Threshold of blistering
1200[b]	Second degree burn
2600[c]	Third degree burn
1060[d]	1% mortality
2300[d]	50% mortality
1100–4000	Piloted ignition of clothing
3000–10000	Unpiloted ignition of clothing

[a] There is evidence for a region of constant injury between these limits.
[b] Second degree burns with a burn depth of 0.1 mm. This value is approximately the same as that for 1% mortality. Burn depth increases linearly up to a thermal load value of 2600.
[c] Third degree burns with a burn depth of 2 mm. This value is approximately the same as that for 50% mortality.
[d] Values based on the probit equation of Eisenberg, Lynch and Breeding (1975).

The *Green Book* also gives relations for non-fatal injury. For first degree burns

$$Y = -39.83 + 3.02 \ln(tI^{\frac{4}{3}}) \qquad [16.22.13]$$

and for second degree burns

$$Y = -43.14 + 3.02 \ln(tI^{\frac{4}{3}}) \qquad [16.22.14]$$

16.22.18 Lees model

Another model for injury by thermal radiation has been developed by Lees (1994a). The model is essentially a set of relationships which may be combined in various ways depending on the scenario modelled and which have been utilized by the author to produce a relation for fatal injury from a sudden heat release such as a fireball, subject to defined assumptions. The causative factor is taken as the thermal load $L' = tI^{\frac{4}{3}}$ $([s(W/m^2)^{\frac{4}{3}}]/10^4)$.

For the severity of the burn injury use is made of the relation given in Figure 16.120(a) of Hymes between thermal load and burn depth δ, which is equivalent to

$$\delta = 8.85 \times 10^{-4}(L' - 920) \qquad [16.22.15]$$

For the relationship between burn injury and mortality the data of J.C. Lawrence (1991) given in Table 16.78 are utilized.

The fraction of the body exposed depends on the scenario considered. The base case it taken as an adult wearing light clothing such that the head, neck, hands and lower arms are exposed. From the data given in Section 16.22.10, it can be seen that the fraction exposed is about 10.5% at the front and 9.5% at the back. The total bare skin, or nominal exposed, area is taken as 20%. The corresponding grouping in Table 16.78 is an exposed fraction of 18–22%.

The population considered is that in the age range 10–69 years (12 groups). Then for 18–22% exposure the average mortality P_{ma} given burn injury is

$$P_{ma} = \frac{(0.1 \times 3) + 0.3 + 0.5}{12} = 0.09$$

Table 16.80 obviously applies to a wide range of burn depths. Since it is desirable to be able to reflect the severity of burns, a particular burn depth δ_a is selected as that corresponding to the average mortality P_{ma} of 0.09 just quoted.

It is reasonable to assume that most burns treated are at the less severe end of the range of burn depths. For the case just considered the burn depth corresponding to the average mortality $P_{ma} = 0.09$ is taken as $\delta_a = 0.25$ mm, which from Equation 16.22.15 corresponds to a thermal load $L'_a = 1200\,(W/m^2)^{\frac{4}{3}}\,s/10^{-4}$. This thermal load corresponds to the value for second degree burns given in Table 16.80. The thermal load at which the burn depth and the mortality are zero is given by Equation 16.22.15 as $920\,s\,(W/m^2)^{\frac{4}{3}}/10^4$. Then, by linear interpolation between these two points of burn depth vs thermal load, full depth burn with $\delta = 2.0$ occurs at a thermal load L'_a of $3200s(W/m^2)^{\frac{4}{3}}/10^4$. Similarly, linear extrapolation gives at this thermal load a mortality P_m of 0.64. By further linear extrapolation, $P_m = 1.0$ occurs at a thermal load L' of $4500\,s\,(W/m^2)^{\frac{4}{3}}/10^4$ and an extrapolated, or notional, 'burn depth' δ of 3.17.

The relations between thermal load, burn depth and mortality in this model are then:

Thermal load, L' $(s\,(W/m^2)^{\frac{4}{3}}/10^4)$	*Burn depth, δ* (mm)	*Mortality, P_m*
920	0	0
1200	0.25 ($= \delta_a$)	0.09 ($= P_a$)
3200	2.0	0.64
4500	3.17 (notional)	1.0

The variation of the mortality P_m with burn depth δ may be expressed in terms of the average burn depth δ_a using the relations

$$\delta_1 = \frac{\delta - \delta_l}{\delta_a - \delta_l} \qquad \delta \le \delta_a \qquad [16.22.16]$$

$$\delta_2 = \frac{\delta - \delta_a}{\delta_u - \delta_a} \qquad \delta > \delta_a \qquad [16.22.17]$$

where δ is the burn depth (mm) and subscripts a, l, u, 1 and 2 denote average, lower, upper, first coefficient and second coefficient, respectively. The mortality P_m is then obtained as

$$P_m = \delta_1 P_{ma} \qquad \delta \le \delta_a \qquad [16.22.18]$$

$$P_m = P_{ma} + \delta_2(1 - P_{ma}) \qquad \delta > \delta_a \qquad [16.22.19]$$

The thermal radiation intensity used is the value incident on the person after atmospheric attenuation.

The exposure of the person to this radiation depends on his behaviour. One model of response is that he faces the event for the response time of 5 seconds and then turns his back and runs away. However, as described in Section 16.22.9, there is evidence, on the one hand, of shorter response times but, on the other, of a tendency

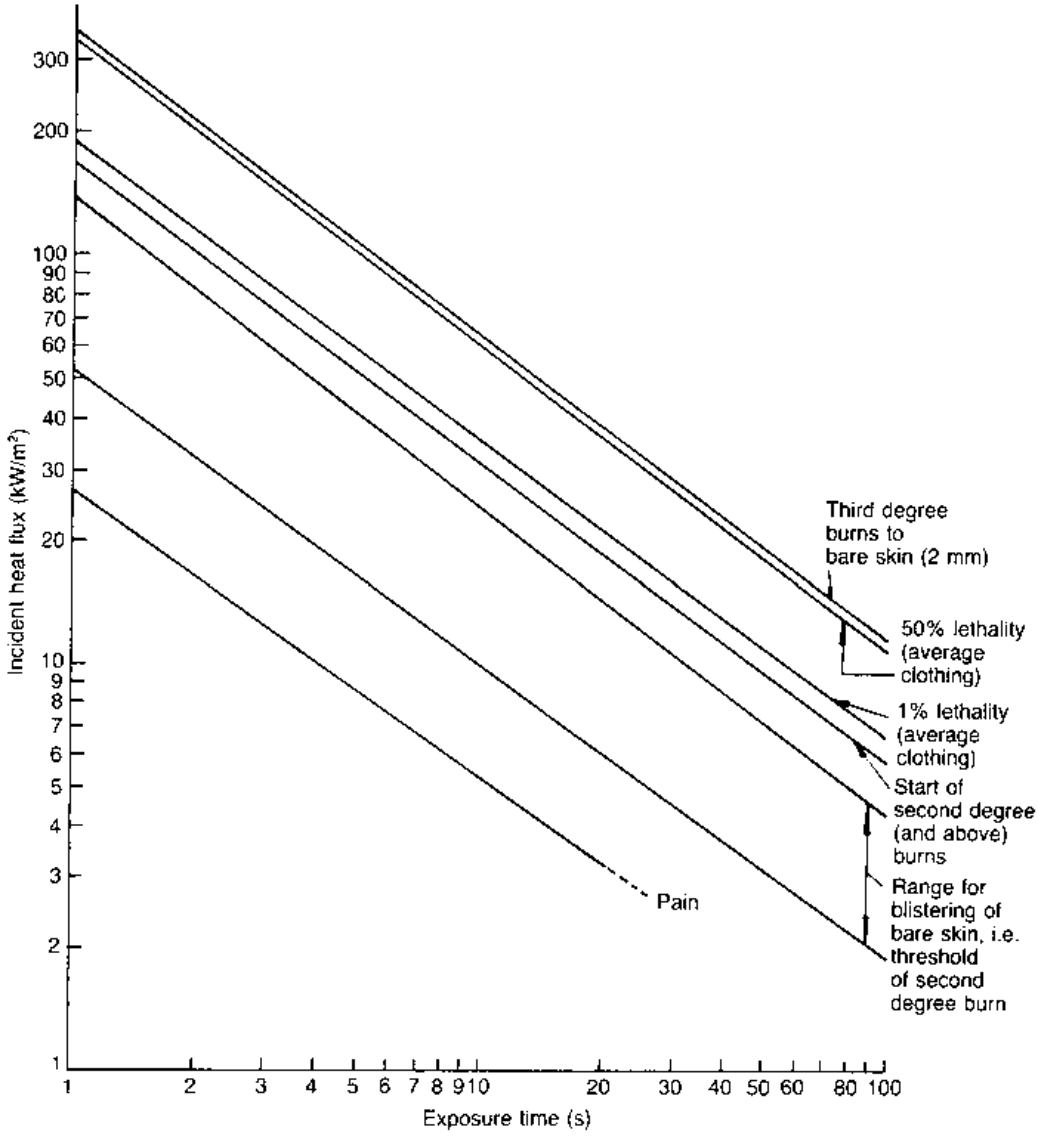


Figure 16.122 *Time to various levels of burn discomfort and injury due to heat radiation (Hymes, 1983 SRD R275) (Courtesy of the UKAEA Safety and Reliability Directorate)*

to turn round to look at the event. From the data given above the fraction of the body exposed when facing the event is greater than that exposed when the back is turned to it, but the difference is not great. The base case adopted is, therefore, that, at least until any clothing ignition, the front and back are equally exposed.

At this stage there are a number of corrections which might be applied. One is for the three-dimensional effect discussed in Section 16.22.12. Another is for the angle of incidence of the radiant heat on the body surface. In the base case a single factor ϕ of 0.5 is used, which takes account of the fact that only about half the bare skin is exposed to the thermal radiation at a given time. This factor is applied to the time t in the thermal load expression, which thus becomes $\phi t I^{\frac{4}{3}}$ so that a given thermal load applied to half the exposed surface over a given time interval t is treated as equivalent to half that load applied to the whole exposed surface over the same time interval.

For clothing ignition correlations have been developed using different 'thermal loads'. One of those used by Hymes is the regular thermal load $tI^{\frac{4}{3}}$ and it is this which is utilized. With respect to the load at which clothing ignition occurs, the value adopted corresponds to the

middle value of the range of 'load' given in the *Green Book*. Thus from Equation 16.22.8

$$tI^2 = 3.5 \times 10^4 \text{s}(\text{kW/m}^2)^2$$

which for a 5 second pulse gives an intensity $I = 84\,\text{kW/m}^2$ and a thermal load

$$L' = tI^{\frac{4}{3}} \approx 1800\ \text{s}(\text{W/m}^2)^{\frac{4}{3}}/10^4$$

Table 16.81 *Lees model for burn injury from a sudden fire event such as a fireball (Lees, 1994a): mortality as a function of thermal load (Courtesy of the Institution of Chemical Engineers)*

Thermal load, L' $([\text{s}\,(\text{W/m}^2)^{\frac{4}{3}}])/10^4)$	*Burn depth,* δ (mm)	*Mortality,* P_m (%)	*Mortality (Eisenberg)* (%)
1000	0.07	0.025	0.015
1200	0.25	0.09	0.04
1400	0.42	0.14	0.09
1600	0.60	0.20	0.16
1800	0.78	0.26	0.24
2000	0.96	0.31	0.33
2500	1.4	0.45	0.55
3000	1.84	0.59	0.73
3200	2.00	0.64	0.78
4500	3.17 (notional)	1.0	0.95

Clothing ignition is taken in the model as resulting in the doubling of the effective exposed area. Following such ignition, therefore, this area is taken as the nominal exposed area. Thus from this point the factor ϕ has a value of unity.

Table 16.81 shows for this model the burn depth and the mortality as a function of the thermal load. The probit equation for fatal injury obtained from these data is

$$Y = -10.7 + 1.99\ln L' \qquad [16.22.20]$$

where L' is the thermal load $([\text{s}\,(\text{W/m}^2)^{\frac{4}{3}}]/10^4)$.

This probit equation is based on the mortality values given in Table 16.81, except the last value of 1.0. As described above, in the model a thermal load of 4500 is taken as corresponding to a mortality of unity. Therefore the probit equation is used only up to a mortality of 70%, and the following relations are used thereafter:

$$P_m = 0.70 + 0.0003(L' - 3500) \qquad L' < 4500 \qquad [16.22.21a]$$

$$P_m = 1.0 \qquad L' \geq 4500 \qquad [16.22.21b]$$

Also shown in Table 16.81 for comparison are the mortalities predicted by Equation 16.22.9 of Eisenberg, Lynch and Breeding. Apart from those at very high thermal loads, the values are not greatly different. The difference between the method of these authors and that

Table 16.82 *Lees model for burn injury from a sudden fire event such as a fireball (Lees, 1994a): illustrative example of mortality from a 20 te LPG fireball (Courtesy of the Institution of Chemical Engineers)*

A Physical conditions

Distance (m)	*Thermal radiation intensity* (kW/m^2)		*Thermal load factor,* L'/t	*Time to ignition,* t (s)	*Thermal load* $(\text{s}\,(\text{W/m}^2)^{\frac{4}{3}}/10^4)$		
	Crude, I	*Attenuated,* I_e	$((\text{W/m}^2)^{\frac{4}{3}}/10^4)$		*Before ignition*	*After ignition*	*Total,* L'
75[a]	390						
95[(b)]	240	173	964	3.73	1800	6044	7844
105	197	142	738	4.89	1800	3771	5571
115	164	118	577	6.24	1800	2169	3969
125	139	97	444	8.11	1800	839	2639
135	119	83	361	9.97	1800	54	1854
145	103	72	298	N	(1490)	N/A	1490

B Thermal injury

Distance (m)	*Clothing ignition*	*Mortality* P_m (%)	*Mortality (Eisenberg)* (%)
75[a]	Y	1.0	1.0
95[b]	Y	1.0	1.0
105	Y	1.0	1.0
115	Y	0.84	0.99
125	Y	0.49	0.95
135	Y	0.23	0.86
145	N	0.12	0.72

[a] Radius of spherical fireball.
[b] Radius of hemispherical fireball.

of Lees lies in the treatment of the effective exposed area.

In Section 16.15 an account has been given of the fireball model by V.C. Marshall (1987). Table 16.82 illustrates the application of Lees' model to the case of the 20 te fireball considered by this author. For this fireball the spherical radius is 75 m, the hemispherical radius 95 m, the duration 10.3 s and the crude thermal radiation intensity $2.17 \times 10^9/x^2$ W/m^2, where x is the distance from the centre of the fireball to the target. In the calculation underlying the data in Table 16.82, use was made of the atmospheric attenuation factors given by Marshall and the fireball duration time was rounded to 10 s. Also shown in the table are the predictions of mortality from the Eisenberg probit applied to the unadjusted thermal loads for the full duration time of 10 s. In his discussion of the rotational factor, Marshall suggests that whereas the Eisenberg probit gives for a such a fireball a distance of 170 m to 50% mortality,

Table 16.83 *Some limits for thermal radiation*

A Design guidance: **IP *LPG Storage Code* 1987**

See Table 22.8

B Design guidance: API RP 510: 1990

Thermal radiation intensity (kW/m^2)	*Limit*
15.6	Intensity on structures where operators are unlikely to be performing and where shelter is available
9.5	Intensity at design flare release at locations to which people have access and where exposure would be limited to a few seconds for escape
6.3	Intensity in areas where emergency actions lasting up to 1 minute may be required without shielding but with protective clothing
4.7	Intensity in areas where emergency actions lasting up to several minutes may be required without shielding but with protective clothing
1.6	Intensity at design flare release at locations where people are continuously exposed

C Design guidance: Kletz (1980h)

Thermal radiation intensity (kW/m^2)	*Limit*
38	Intensity on storage tanks
12.5	Intensity on wood or plastics[a]
5	Intensity on people performing emergency operations

D Design and assessment guidance – BS 5980: 1990[b]

Thermal radiation intensity (kW/m^2)	*Limit*
37.5	Intensity at which damage is caused to process equipment
25	Intensity at which non-piloted ignition of wood occurs
12.5	Intensity at which piloted ignition of wood occurs
4.5	Intensity sufficient to cause pain to personnel unable to reach cover in 20 seconds, though blistering of skin (first degree burns) unlikely
1.6	Intensity insufficient to cause discomfort for long exposures

E Design and assessment guidance: Mecklenburgh (1985)

Thermal radiation intensity (kW/m^2)	*Limit*
14	Intensity which normal buildings should be designed to withstand
10–12	Intensity at which vegetation ignites
6	Intensity tolerable to escaping personnel
3	Intensity tolerable in infrequent emergency situations of up to 30 minutes duration
1.5	Intensity safe for stationery personnel and members of the public

F Assessment guidance: Dinenno (1982)

Thermal radiation intensity (kW/m^2)	*Limit*
30	Spontaneous ignition of wood
15	Piloted ignition of wood
20	Ignition of No. 2 fuel oil in 40 seconds[c]
10	Ignition of No. 2 fuel oil in 120 seconds[c]
18–20	Cable insulation degrades[d]
12	Plastic melts[e]
37.5	Equipment damage[f]
9	Equipment damage[f]

[a] Kletz comments that the implication of this limit is that large storage tanks need to be located at least 200 m from public roads.
[b] BS 5908: 1990 also gives a thermal dose of 600–1800 kJ/m^2 from a fireball as a criterion for the starting of secondary fires.
[c] EPRI (1981a).
[d] EPRI (1979b).
[e] Gelderblom (1980).
[f] Di Nenno comments that there is significant variation in the thresholds for equipment damage. He gives the source of the value of 37.5 kW/m^2 as Gelderblom (1980), and treats the value of 9.5 kW/m^2 given by Tan (1967a), in relation to flare system design, as conservative.

experience of incidents indicates this is much too far, and he tentatively suggests that the distance of about 90 m given by assuming rotation through 360° is closer to reality. From the table, Lees' model gives a distance of 125 m. Lees states that his model, whilst not intended to be conservative and whilst less so than the Eisenberg relation, may nevertheless still be so.

16.22.19 Prugh model

A model for burn injury from exposure to a fireball has been given by Prugh (1994). He presents a summary of data on burn injury, which for fatality draws on the work of Eisenberg, Lynch and Breeding (1975), Lees (1980b), A.F. Roberts (1982) and the Society of Fire Protection Engineers (1988 NFPA/22). From these data he derives the following correlation for the probability P of fatality:

$$P = \{1 + [1 - (\exp\{-5.3[\ln(E/53)]^2\}]^{0.5}\} \times [1 - 2(E/53)] \quad [16.22.22]$$

where E is the thermal dose (J/m^2). He presents a graphical comparison of this equation with the two *Green Book* relationships for unprotected and protected exposure, which shows that the mortalities predicted by his correlation are appreciably lower.

With regard to the extent of the burns and to medical treatment, Prugh gives a graph of mortality vs fraction of the body with third degree burns, based on the data of J.W. Davies (1982), but states that such treatment is presumably already taken into account in the basic mortality data which he uses.

Combining the fireball model and the injury relationships, Prugh derives for a propane fireball a graphical correlation for mortality, which is a function of the mass of fuel and the distance of the person exposed. He also gives equations, which are considered in Section 16.39.

16.22.20 Thermal radiation limits

There are a number of empirical limits of thermal radiation which have traditionally been used in plant design. Other limits are quoted in work on hazard assessment. Some of these limits are quoted in Table 16.83.

16.23 Fire Protection of Process Plant

In general, fire prevention and protection measures constitute either (1) passive prevention and protection or (2) active protection.

Reference has already been made to some principal publications on fire in relation to process plants, but it is appropriate to refer here to *Practical Fire Protection* (Underwood, 1971–) and *Underwood's Practical Fire Protection* (Hirst, 1989), *Fire Protection Manual for Hydrocarbon Processing Plants* (Vervalin, 1964a, 1973a), *Storage and Handling of Petroleum Liquids: Practice and Law* (J.R. Hughes, 1970), to the NFPA codes and to BS 5908: 1990 *Code of Practice for Fire Precautions in the Chemical and Allied Industries.*

16.23.1 Passive fire protection

Passive prevention and protection comprises measures which are taken in order to prevent a fire occurring and to limit its spread. Measures of active protection comprise fixed and mobile fire fighting systems and emergency arrangements.

As a broad generalization, passive fire protection has the great advantage that it is very much less dependent on the intervention of protective devices or of humans, both of which are liable to fail, and is therefore that much less vulnerable to management failings.

One of the principal passive fire protection measures is fireproofing. In general this has the advantages just mentioned. But it also brings with it the risk that corrosion may occur under the fireproof coating and may be difficult to detect. Another problem with fireproofing is the fact that it may not withstand the action of the powerful water jets used in fire fighting.

Insofar as management has some control over both these features – the avoidance of corrosion and of loss of coating by water jets – they illustrate the fact that even the use of passive fire protection measures does not avoid the need for good management.

The optimum solution to the fire protection problem is normally a combination of passive and active measures. Often passive fire protection can limit fire spread and can 'buy time' in which the fire fighting resources can be mobilized.

16.23.2 Active fire protection

Active fire protection measures are also provided in the basic plant design, but are effective only when activated in response to a fire. Elements of active fire protection are:

(1) fire warning systems;
(2) fire detection systems;
(3) fire fighting agents;
(4) fire water supply system;
(5) fixed fire fighting systems;
(6) mobile fire fighting systems.

Item (1) of these measures is described in Chapter 24 and item (4) in Chapter 10, while the other items are dealt with below.

16.23.3 Fire detection and alarm

The initiation of active fire protection measures, whether fixed systems or mobile fire fighting systems, depends on the fire detection and alarm arrangements.

Accounts of fire detection and alarm are given by Fry and Eveleigh (1975 BRE CP 32/75) and P. Nash and Young (1975 BRE CP 29/75). Treatments of water sprinkler and water spray systems also frequently deal with detection systems.

Relevant codes and standards are the NFPA 72 series, particularly NFPA 72E: 1990 *Automatic Fire Detectors*, BS 5445: 1977 – *Components of Automatic Fire Detection Systems*, BS 5839: 1988 – *Fire Detection and Alarm Systems for Buildings* and, until recently, BS 6020: 1981 – *Instruments for the Detection of Combustible Gases*, now superseded by the series BS EN 50054–50058 which has the general title *Electrical Apparatus for the Detection and Measurement of Combustible Gases*.

When a fire occurs, two things which are of prime importance are to ensure the safety of personnel and the prompt initiation of action to deal with the fire. The most effective way of ensuring rapid action is generally the use of an automatic system. But in situations where

personnel may be present the arrangements need to ensure that they are not put at risk by the action of the automatic system.

There are several different types of system for the detection of leakage and/or fire. They may be classified according to whether they detect (1) leakage, (2) flame, (3) heat or (4) smoke. These systems and the devices used are listed in Table 16.84.

In general, it is preferable to detect a leakage in its initial stages and before it ignites. On the other hand, some types of fire, such as lagging fires, are not preceded by readily detectable leakage.

The alternative is to detect the fire itself. This is done most rapidly by flame detection. Detection of the heat and smoke from the fire is possible only after it has developed to some extent.

Some important characteristics of detection systems are:

(1) area covered;
(2) response time;
(3) reliability –
    (a) fail-to-danger faults,
    (b) fail-safe faults (spurious alarms);
(4) cost.

The area covered by a detection device is important, because a small coverage leads to a complex and expensive system. The reliability is also important both in respect of fail-to-danger faults and of fail-safe faults which cause spurious alarms.

Detection of abnormal conditions, including leakage and fire, is a basic function of the process operator. He is capable of detecting such conditions by all the modes described and gives wide coverage with high reliability and low cost. His great disadvantage is that he may not respond rapidly enough, not only in making the initial detection but also in initiating fire fighting action.

Instrument detection systems are therefore widely used. In many cases they are part of a fully automatic system which triggers protective devices such as steam curtains, or releases fire fighting agents. In other cases, however, the function of the detection system is limited to providing an alarm signal to the operator, which he then has to interpret. There are several reasons for not always making the system fully automatic. One is that detection systems are liable to give spurious alarms; another is that it is not always easy to define in advance precisely what is required. It is often difficult, for example, in an automatic water spray system to avoid wasting water in cooling plant where this is not really necessary. This is important, because the quantities of water required for water sprays are large.

The most widely used type of system is the combustible gas detection method. Descriptions are given by several authors (e.g. Bossart, 1974; Dailey, 1976; Johanson, 1976). There are two main types of combustible gas detection. One consists of a number of devices which sample the atmosphere at different points and pass the sample back to a common analyser. Typical sample pipe velocities are 3 m/s and sampling rates 10–30 s per point.

There are a variety of instruments available for combustible gas analysis, based on the measurement of the heat produced by a catalytic reaction, radiant energy, absorption, ionization phenomena, electrochemical effects, colorimetric effects and gas chromatography. Details are given by Dailey.

Table 16.84 *Some detection systems for fire protection*

Basis of detection	*Detector*
All modes	Humans
Leakage	Flammable gas detector
Flame	Infrared detector
	Ultraviolet detector
Heat	Temperature measuring instrument
	Quartz bulb detector
	Gun cotton bridge and wire
	Fusible link and wire
	Temperature sensitive resistor
	Air line
Smoke	Smoke detector

A single instrument system is, in general, most appropriate where the analyser itself is very complex and expensive and where some time delay is acceptable. These characteristics appear to make it more suitable for detecting toxic gases which pose a long-term hazard, but less so for detecting flammable gases, where the analytical instruments are comparatively simple but fast response is important. Common analyser systems have in fact been subject to severe criticism by some users (e.g. Kletz, 1976i) as being excessively slow in response and liable to faults such as blockage.

The other system, which is preferred by such users, utilizes an individual catalytic diffusion type detector at each detection point. Generally, a combustible gas detector is installed and calibrated for one particular hydrocarbon gas, but will respond to others. The instrument scale is usually calibrated as 0–100% of the lower explosive limit (LEL). The output of a detector calibrated on propane will read some 20% high on methane and some 20% low on propylene.

Catalytic detectors are susceptible to poisoning. In particular, silicone grease and silicone rubber sealants have been found harmful. Combustible gas detector instruments should be regularly serviced. Portable detectors should be checked before use.

There tends to be some trade-off between the speed of response and the number of spurious signals obtained. It is suggested by Johanson that the specification for response time is generally too tight and that an allowance of a few seconds delay reduces the number of false alarms.

There are various approaches to laying out the detection points. Generally, it is desirable to have detectors around the periphery. Other detectors are then sited according to principles such as uniform coverage, location at leak sources, location between leak and ignition sources.

The optimum height of the sample point depends on the density of the gas. Johanson suggests installation at $1\frac{1}{2}$ and 6–8 ft for heavy and light gases, respectively. It is also necessary to take into account depressions, roofed areas and other pockets.

A combustible gas leakage detection system may be used to provide alarm signals in the control room or to initiate protective action by water sprays or by a steam curtain.

Detection of a flame is done by infrared or ultraviolet detecting instruments. The response time of the former is generally about 10 seconds, while with the latter it is almost zero. The reliability of these relatively complex instruments is a problem, particularly, although not exclusively, because they tend to give frequent false alarms, but there has been considerable improvement in this aspect. The instruments are also comparatively expensive. Again a flame detection system may be used to give alarm signals or to trigger water sprays.

There are a number of devices which detect heat. They include temperature measuring instruments, quartz bulbs, and devices which explode, melt or change characteristics when exposed to fire. The latter include gun-cotton bridges and wire, fusible links and wire, air lines which melt through, and resistors which change resistance. Measuring instruments can be used to furnish alarm signals or to set off water sprays, but the other devices are generally used for the latter purpose. Thus a simple detection system might be based on an air line which can be melted through by a fire so that the air pressure in the line falls, allowing the drench valve on the water spray system to open.

A quartz bulb detector figured prominently in the Flixborough inquiry (R.J. Parker, 1975, pp. 20–26, especially paragraphs 137, 156, 157 and 160, and Figure 8). According to the 8 in. pipe hypothesis, a fire occurred at a non-return valve in a lagging box. There was believed to be a quartz bulb some 12 in. above the top of the valve and some 18 in. to the east which was set to actuate a water spray system at a temperature of 68°C or above. It was a matter of dispute whether there could have been a fire at the lagging box without activation of this detector. Proponents of the 8 in. pipe hypothesis argued that either there was no quartz bulb or that it did not operate. Calculations were done which were said to show that heat radiation from the assumed flame would not be enough to trigger the detector and that heat radiation from the pipework would be necessary to do this. The assessors considered, however, that if the hypothesis were correct the sensor would have been triggered by other flames and radiating surfaces present. In any event, the water spray system apparently did not operate. These points are of some importance, because they bear on the effectiveness of detector systems. Further discussion of the matter is given by J.I. Cox (1976b).

Another method of detecting fire is by smoke detectors. These are widely used in buildings, but appear likely to be less effective for fires on open plant.

16.23.4 Emergency material transfer

It is necessary to have arrangements so that in the event of fire it is possible to transfer flammable material away from the parts of the plant affected. Provision of a relief header leading to a vent stack or flare stack allows vapour to be vented safely from pressure vessels. The removal of liquid from a pressure vessel may be catered for by facilities for blowdown to a suitable receiver. Similarly, pumps may be installed on atmospheric storage tanks to allow liquid to be transferred out.

16.23.5 Dow Fire and Explosion Index

The Dow Fire and Explosion Index given in the Dow *Guide* has been described in Chapter 8, where the method of calculating the index was outlined. The purpose of the index is to assist in the selection of preventive and protective features.

The following set of preventive and protective features are listed in the Fourth Edition of the *Guide* (Dow Chemical Company, 1976): (1) basic preventive and protective features and (2) recommended minimum preventive and protective features. The latter features are not given as such in the later editions, but the Fifth Edition introduces loss control credits, which cover similar ground, and also an engineer's checklist. Table 16.85 lists the basic preventive and protective features given in the Seventh Edition (Dow Chemical Company, 1994) and Table 16.86 lists the headings of the recommended minimum preventive and protective features in the Fourth Edition.

The features shown in Table 16.85 should always be provided, irrespective of the degree of hazard. If they are not, the hazard will be greater than that calculated by the index. Many of them apply in any plant, regardless of whether it contains flammable materials. It should be noted that the codes and electrical area classification mentioned in Table 16.85 are those applicable in the USA.

Table 16.86 lists headings of the features which should always be considered where a fire or explosion hazard exists. The detailed measures under these headings are described in the *Guide*. The features are intended to reduce the magnitude and/or the probability of the loss. The need for a particular feature depends on the nature of the hazard.

The Dow Fire and Explosion Index is widely used as an aid to the selection of fire preventive and protective features, and is therefore a relatively well proven method. Nevertheless, it is a generalized method and, if used, it should be supplemented by specific hazard identification and assessment studies which may reveal the need for other preventive and protective features.

16.24 Passive Fire Protection

The previous section has given an account of the general nature and purpose of passive fire protection. In this section specific passive fire protection measures are considered.

Measures of fire prevention and passive fire protection are built into the basic plant layout and design. They include such aspects as:

(1) elimination of fires –
  (a) leaks and spillages,
  (b) sources of ignition;
(2) emergency material transfer –
  (a) pressure relief and flaring,
  (b) blowdown,
  (c) dumping;
(3) fire spread limitation;
(4) fire protective insulation –
  (a) fire resistant thermal insulation,
  (b) fire insulation;
(5) storage tank layout.

Table 16.85 *Dow Guide: Basic Preventive and Protective Features (Seventh Edition) (Dow Chemical Company, 1994; reproduced with permission)*

A	Adequate water supply for fire protection. This is determined by multiplying the water demand by the length of time for which the worst possible fire can be expected to last. The supply deemed adequate will vary with different authorities and may range from enough for a 2-hour fire to enough for one lasting 8 hours
B	Structural design of vessels, piping, structural steel, etc.
C	Overpressure relief devices
D	Corrosion resistance and/or allowances
E	Segregation of reactive materials in process lines and equipment
F	Electrical equipment grounding
G	Safe location of auxiliary electrical gear (transformers, breakers, etc.)
H	Normal protection against utility loss (alternate electrical feeder, spare instrument air compressor, etc.)
I	Compliance with various applicable codes (ASME, ASTM, ANSI, Building Codes, Fire Codes, etc.)
J	Fail-safe instrumentation
K	Access to area for emergency vehicles and exits for personal evacuation
L	Drainage to handle probable spills safely, plus fire fighting water from hose nozzles and sprinkler heads and/or chemicals
M	Insulation of hot surfaces that heat to within 80% of the auto-ignition temperature of any flammable in the area
N	Adherence to the National Electrical Code. The Code should be followed except where variances have been requested/approved
O	Limitation of glass devices and expansion joints in flammable and hazardous service. Such devices are not permitted unless absolutely essential. Where used, they must be registered and approved by the production manager and installed in accordance with Dow standards and specifications
P	Building and equipment layout. Separation of high-hazard area must be recognized especially as it relates to both property and interruption of business. Separation of tanks must be at least in accordance with NFPA 30
Q	Protection of pipe racks and instrument cable trays as well as their supports from exposure to fire
R	Provision of accessible battery limit block valves
S	Cooling tower loss prevention and protection
T	Protection of fired equipment against accidental explosion and resultant fire
U	Electrical classification. Division 2 electrical equipment will be required for outside flammable liquid handling where congestion is minimal and natural ventilation is unobstructed. Division 1 equipment is required only for special chemicals and/or special building or process handling conditions or where ventilation is inadequate
V	Process control rooms shall be isolated by 1 hour fire walls from process control laboratories and/or electrical switchgear and transformers
W	A process review shall determine a need for reactive chemicals testing
X	A hazard and operability (hazop) review is recommended in high hazard areas

Table 16.86 *Dow Guide: Minimum Preventive and Protective Features (Fourth Edition) (Dow Chemical Company, 1976) – these features are listed in the Guide which gives a detailed description of them*

1	Fireproofing
2	Water spray protection of equipment and area
3	Foam or filming agents
4	Monitor guns
5	Dump, blowdown or spill control
6	Combustible gas monitors
7	Diking for storage tanks
8	Buried tanks
9	Foam on tanks
10	Remote manual control
11	Special instrumentation
12	Fire walls and barrier walls/cubicles
13	Building ventilation
14	Dust explosion control
15	Open process structure
16	Emergency relief venting for buildings

Of these measures, items (1) and (2) have been dealt with already in this chapter and item (5) is considered in Chapters 10 and 22. The other items are described below.

16.24.1 Fire spread limitation

There are certain plant configurations which assist fire spread. By avoiding or modifying these configurations, fire spread may be limited.

Two examples given by Klootwijk (1976) are shown in Figure 16.123. In a fire a chimney effect can develop in the space between a table top and a tall equipment or structure as illustrated in Figure 16.123(a). Such an effect tends to increase damage and to extend it to a higher level. Where a potential chimney cannot be avoided, it may be appropriate to install a water spray system to control fire in the area.

A chimney effect can also occur between a table top and the bottom of a large column. In this case the opening should be closed off with a support skirt, as shown in Figure 16.123(b).

Another way in which fire can spread is by the flow of a burning liquid. The plant layout with regard to this aspect should be carefully considered. It is normal practice to put bunds around storage tanks. But there may be other situations which can give rise to liquid flow. Drains, sewers and pipe trenches are features which are particularly liable to aggravate this hazard.

16.24.2 Fire resistant thermal insulation

Many items of equipment are fitted with thermal insulation. This is to be distinguished from fire insulation proper. Nevertheless, provided it is of the right type, thermal insulation can provide a degree of fire protection. Much process plant is thermal insulated, as are low temperature storage tanks.

The fire resistant properties of regular thermal insulation are considered in Chapter 12. The fire protection offered by such insulation on storage tanks is discussed in Chapter 22.

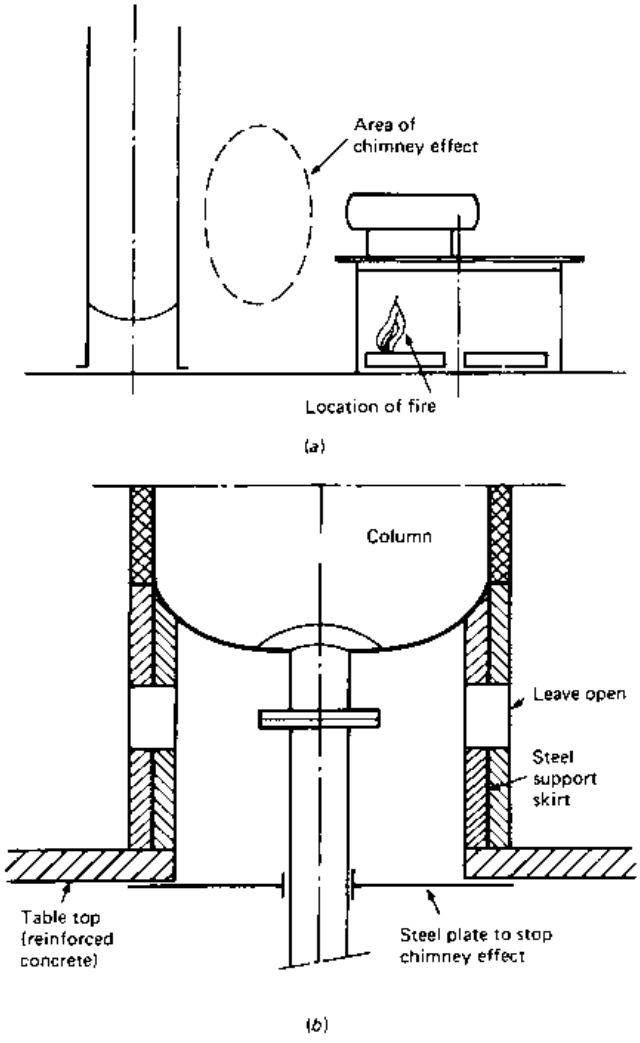


Figure 16.123 *Fire spread and its limitation (Klootwijk, 1976): (a) chimney effect between table top and a tall structure; (b) elimination of the chimney effect between a table top and the bottom of a column by use of a steel support skirt*

16.24.3 Fire insulation

Some form of structural protection against fire, in the form of fire insulation or fireproofing, is normally provided for supporting members, and also for vessels and pipework. A general account of fireproofing has been given by Waldman (1967).

Factors which need to be taken into account in considering such fireproofing include:

(1) protection criteria –
  (a) type of structure,
  (b) height of structure,
  (c) degree of protection;
(2) fireproofing system.

There are differences of practice in the types of structure which are fireproofed. The main emphasis is generally on the protection of supporting members. Fireproofing is sometimes limited to supports of major items such as large columns or vessels, but it is often extended to supports of other items, such as heat exchangers and pipework. In some cases it is applied to the vessels and pipework themselves.

The main object of fireproofing is to prevent the failure in a fire of items containing flammable material which can feed the fire. Fireproofing may not be needed, therefore, for items with a small inventory, unless failure could lead to large loss of containment from some other source.

The height above grade, or ground level, to which the protection extends is also variable. Most fires do not reach much more than 10 m above grade, although there have been instances of damage at heights of 30 m or

more. It is suggested by Waldman that fireproofing should extend to 35 ft (10 m) above grade.

It is also necessary to decide on the degree of protection required. A common criterion is that the steel member should not reach a temperature greater than 1000°F (538°C) under specified fire conditions.

In deciding on the degree of protection required for fireproofing, allowance may be made for other fire protection features, such as water sprays. It is the whole fire protection system which matters. In general, the aim should be to prevent a fire occurring at all near a vulnerable structure. It is better to provide drainage to take the flammable liquid away.

A fireproofing system normally consists of a bulk insulation material which gives protection against fire. This bulk fire insulation may be clad with aluminium, galvanized or stainless steel sheet. Such fire insulation should be distinguished from conventional insulation which is used to reduce heat transfer between the plant and the atmosphere. Such insulation may or may not have fire resistant properties. Materials which are widely used as the bulk fire insulation include (1) concrete and (2) magnesium oxychloride cement. Concrete is often used in the form of lightweight aggregate concrete, or vermiculite cement.

Protection against fire may also be obtained by the use of a mastic, which may be asphaltic or vinyl acrylic. Mastics are used to fireproof not only plant but also conventional insulations. Some materials used as the bulk fire insulation have special fire resistant properties. Magnesium oxychloride, for example, contains water of crystallization, which takes up heat when it is driven off. Similarly, some coating materials have properties which increase their effectiveness in fireproofing. Intumescent mastics swell in fire by a factor of 5–10 and this gives increased insulation.

Some features of a fireproofing system include:

(1) insulation properties;
(2) mechanical strength;
(3) corrosion –
    (a) substructure,
    (b) reinforcing;
(4) water penetration;
(5) flexibility;
(6) weight;
(7) ease of installation;
(8) cost.

Fireproofing should provide sufficiently effective insulation to keep the temperature of the structural member to be protected below a specified temperature under defined fire conditions. It has been suggested by Kayser (1974) that the ideal system will hold the substrate below 1000°F (538°C) for $1\frac{1}{2}$ hours while its surface is exposed continuously to a temperature of 1800°F (982°C). The maximum substrate temperature of 1000°F is that widely quoted, but the maximum period of protection is generally less. Thus Waldman suggests, for example, that in order to allow for spray failure protection is required for 1 hour. This time period is also quoted by other workers, as described below.

The mechanical strength of the fireproofing should be sufficient to offer reasonable resistance to damage both from normal plant activities and from water from fire hoses.

The bulk fire insulation should not be corrosive to the substrate or to the reinforcing material. The substrate should be made clean and rust free before the insulation is put on.

It is essential that water should not be allowed to penetrate the insulation and corrode the substrate or the reinforcing material. Corrosion of the steel structural members is difficult to detect, but could have serious results. The coating or cladding used should therefore offer complete protection, particularly at horizontal surfaces where water may get in.

The insulation should be able to accommodate, without cracking, the expansion and contraction of the structure protected. Other desirable features are light weight, ease of application and low cost.

A fireproofing system which is widely used is concrete with galvanized steel sheet cladding (Klootwijk, 1976). Vermiculite cement and magnesium oxychloride cements are also much utilized.

Some illustrations of fireproofing of structural supports are shown in Figure 16.124.

16.24.4 Tests for fire insulation

There is frequently a requirement to test a proposed fireproofing system. Unfortunately, there is no standard test appropriate to structural elements in a flammable liquid fire, which is the typical situation in process plant. Many experimenters have resorted, therefore, to the ASTM E-119 standard time–temperature test, which was devised for building fires. The test involves maintaining the element in a standard fire in which the temperature rises along the standard curve shown in Figure 16.125, curve 1. The criterion of success is the ability of the element to carry out its original function, in this case fireproofing. The ASTM E-119 test is discussed further in Section 16.36 in relation to its original application to fires in buildings. Most workers have used as the criterion of success the ability of fireproofing to keep the temperature of the steel protected below 1000°F (538°C) for a period of 1 hour.

It has long been recognized that the ASTM curve tends to underestimate the temperatures which occur in fires of hydrocarbons. An early proposal for a higher temperature relation was made by Waldman (1967), who gave two alternative curves.

The unsatisfactory nature of the ASTM E-119 test in this application has been demonstrated by Castle (1974). He emphasizes that in order to assure similarity of test conditions it is necessary to use not only the same temperature but also the same heat fluxes. He presents experimental results which illustrate this point. He also discusses the alternative pool and pit fire tests and states that a pit fire test is generally a more severe one than the ASTM E-119 test.

Since then several other time–temperature curves have gained currency. Two of these are shown in Figure 16.125. Curve 2 is that of the Norwegian Petroleum Directorate (NPD). Curve 3 is generally known as the 'Mobil curve'.

The use of a standard time–temperature curve for hydrocarbon fires leads to an H rating, as opposed to the A rating obtained by using a curve suitable for building fires.

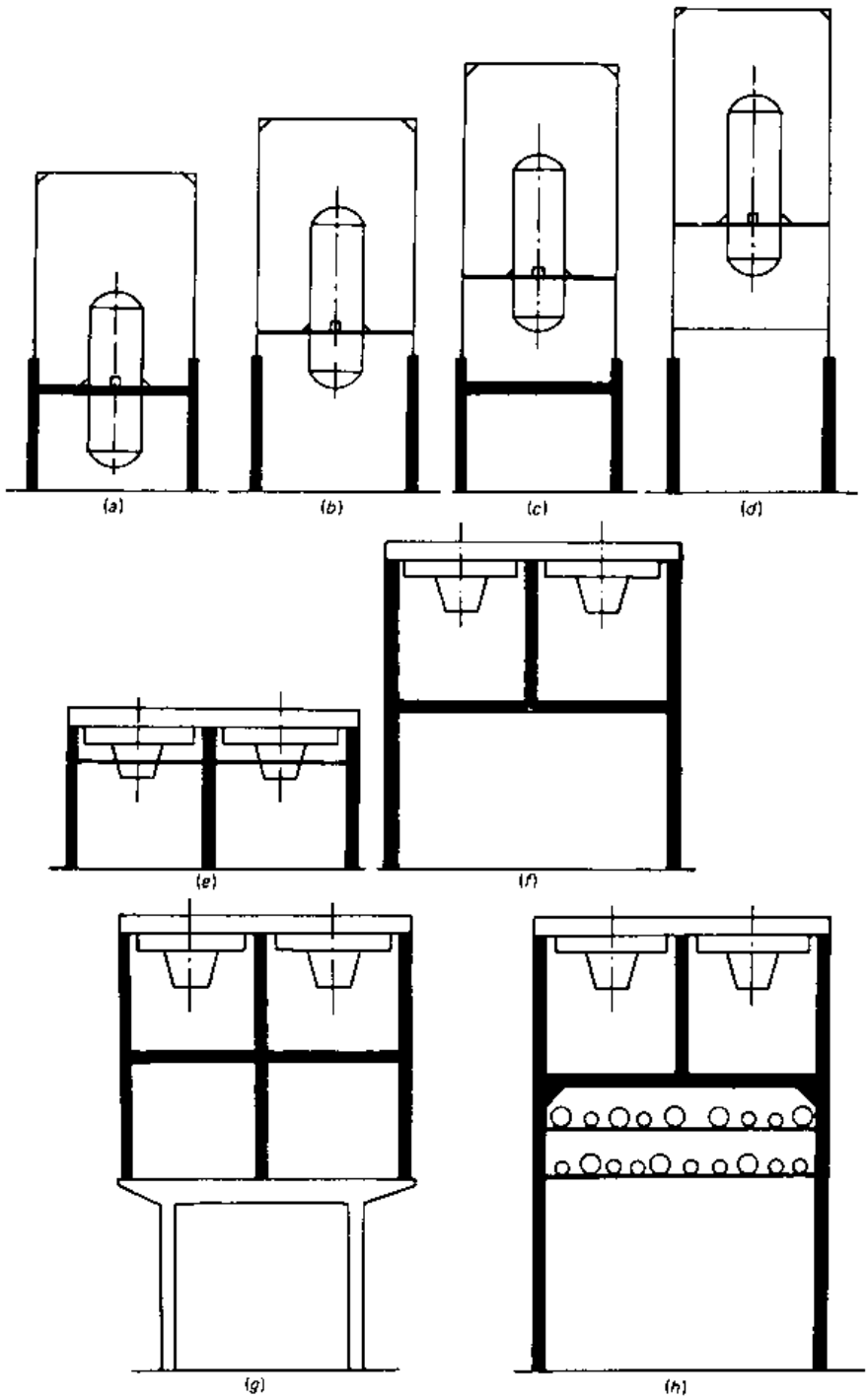


Figure 16.124 *Fireproofing of structural supports (Klootwijk, 1976): (a–d) supporting structure of small storage vessel; (e–g) supporting structure of fin-fan cooler; and (h) supporting structure of fin-fan cooler and overhead pipe track*

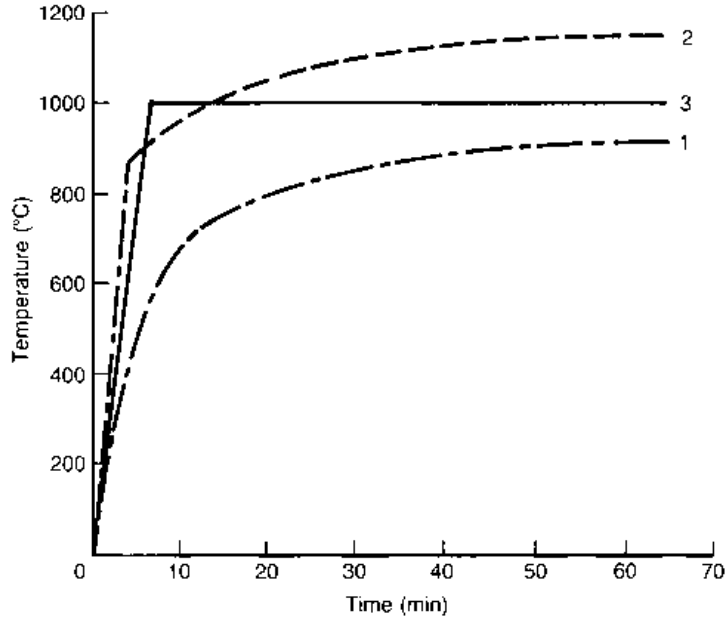


Figure 16.125 *Some time–temperature curves for fires in process plant. Curve 1, ASTM E 119–1988; Curve 2, Norwegian Petroleum Directorate; Curve 3, 'Mobil' curve (after Cullen, 1990)*

Another test which is utilized is the ASTM-84 surface burning test, in which a standard fire is used to evaluate the rate of flame spread across the surface of the element. The latter is rated on a scale on which the points 0 and 100 correspond to asbestos cement and redwood, respectively. An index above 25 is generally regarded as unsatisfactory for fireproofing. The use of this test is described by Feldman (1974).

Much equipment and pipework is provided with insulation which serves primarily to conserve heat or cold in the process. Such insulation is different from that used for fireproofing. But it is important to know what degree of protection against fire it offers.

Experiments on insulations commonly used for pipework have been described by McMillan (1974). The test exposed five insulated pipes of 3 in. diameter to a flame area of approximately 30 ft^2 at temperatures corresponding to the ASTM E-119 time–temperature curve. The minimum fire resistance considered acceptable was taken as maintenance of the pipe temperature below 1000°F (538°C) for 1 hour.

Systems which met this criterion almost exactly included: a 1 in. calcium silicate insulation with a 10 mil (1 mil = 0.001 in.) stainless steel jacket; a 2 in. ceramic foam insulation with vinyl acrylic mastic or asphaltic mastic coating or 10 mil cladding of aluminium or stainless steel; and a 3 in. rigid polyurethane foam insulation with 10 mil vinyl coated steel cladding.

The behaviour of polyurethane foam insulation in fire has been a subject of some controversy. There are a number of different types of polyurethane foam. In a fire, some foams melt, some char, some both melt and char, and some char and rupture, leaving gaps. According to McMillan, however, a suitable polyurethane foam can give good fire resistance. Detailed experimental work on the behaviour of polyurethane foams in fires is described by Boult, Gamadia and Napier (1972) and by Boult and Napier (1972).

Fireproofing is discussed in the ICI *LFG Code* (ICI/RoSPA 1970 IS/74). For pressurized storage vessels the code suggests that one suitable form of fireproofing is vermiculite cement. For the 2 hour protection which is commonly provided, the minimum thickness of vermiculite cement required is 2 in. For refrigerated storage vessels the conventional insulations are cork, polyurethane and perlite powder. The Code discusses the degree of fire resistance offered by these materials and suggests that an additional fireproof finish may be required to give 2 hour fire resistance.

16.24.5 Reactive fire resistant coatings

A quite different method of fireproofing is the use some form of a reactive coating. Accounts of reactive coatings include those by Feldman (1974), O'Rourke (1974), Kawaller (1980), R. James (1988), Gillon (1989) and Droste (1992).

Reactive coating are of three main types: (1) magnesium oxychloride, (2) intumescent coatings and (3) subliming coatings.

Magnesium oxychloride exposed to fire undergoes loss of its combined water so that a porous matrix is formed. It gives a light, hard covering that is resistant to impact, abrasion and weather and provides good fire resistance. A proper formulation should be used; home-made ones can be unsatisfactory. It does, however, have some drawbacks. One is that it requires metal lath reinforcement, another that it is somewhat corrosive so that the

equipment needs to be protected, and a third that it tends to lack adhesion and requires a good 'key'.

Intumescent coatings were first used as paint to retard surface spread of flame. They were so successful that a fire resistant coating was developed. In a fire an intumescent coating releases cooling gases and leaves a residue of thick insulating foam. Tests show that a $\frac{1}{4}$in. layer can give a 1-hour protection. Longer periods of protection can be obtained using thicker layers with reinforcement.

With a subliming compound the principle of operation is that the coating sublimes so that as long as material remains on the surface the temperature of sublimation is not exceeded. The technique was initially developed for aerospace work. Thus subliming coating ThermoLag 330 has been used to protect the structure holding the Saturn rocket at blastoff when temperatures reach 3000°F (1649°C). The coating material itself is expensive, but is relatively cheap to apply.

The use of subliming coating is described by Feldman (1974). He quotes tests conducted on steel beams in an alcohol pit fire with exposure of 1800°F (982°C) for 2 hours. An unprotected beam reached a temperature of 1000°F (538°C) in 10 minutes, whereas a beam protected by subliming coating rose to a maximum temperature of only 500°F (260°C) over the whole period.

Droste (1992) describes two full-scale tests on a 3.6 m^3 LPG vessel protected in one test by the subliming coating ThermoLag 440 and in the other by the intumescent coating Chartek III. The tests demonstrated satisfactory performance of both coatings for full fire engulfment over 90 minutes.

Reactive coatings are lightweight and durable. The applications where they are most likely to be economic are those where alternative softer materials are less suitable. Some practicalities of the use of reactive materials are discussed by Kawaller (1980).

16.24.6 Fire protection of steelwork

Turning to the passive fire protection of particular plant features, protection of structural steelwork is of some importance. Accounts of the fire protection of steelwork include those by Kayser (1974), Klootwijk (1976), Buck and Belason (1985), Latham, Kirby and Thomson (1987), Melinek and Thomas (1987), G.M.E. Cooke (1988) and Melinek (1989).

From standard tests information is available on the time for steel configurations, either uninsulated or with insulation arrangements, to reach a given temperature (e.g. Franssen and Bruls, 1986; API RP 520: 1990). A commonly used criterion temperature is 550°C.

Design guidance for fire protection of steelwork is given in *Designing Fire Protection for Steel Columns* (American Iron and Steel Institute, 1980), *Fire Protection for Structural Steel in Buildings* (CONSTRADO, 1983) (the *Yellow Book*) and *Design Manual on the European Recommendations for the Fire Safety of Steel Structures* (ECCS, 1985) and by Law (1972, 1991), Barnfield (1986) and Melinek (1989).

There are a number of models for predicting the times required to attain particular temperatures for insulated steelwork in a fire, including those by the European Convention for Constructional Steelwork (ECCS) (1985) and the National Research Council of Canada (NRCC) and by Wickström (1981/82, 1985) and Melinek (1989).

In estimating these times it is also necessary to define the nature of the fire to which the steelwork might be exposed.

16.24.7 Fire resistant valves

Valves are another type of equipment for which good fire resistance is highly desirable. Fire resistant, or fire safe, valves are available. Accounts of fire resistant valves are given by J.B. Wright (1981) and Cory and Riccioli (1985).

Relevant standards are API Std 589: 1993 *Fire Test for Evaluation of Valve Stem Packing*, API Spec. 6FA: 1994 *Specification for Fire Test for Valves* and BS 6755: *Testing of Valves*, Part 2: 1987 *Specification for Fire-Type Testing Requirements*, which replaces the earlier BS 5146: 1974–.

Interest centres particularly on the fire resistance of ball valves.

Among the features listed by J.B. Wright (1981) as being evaluated in tests are: operability whilst hot, leakage behaviour in a rapidly controlled fire and in a more prolonged one, and ability to withstand/relieve cavity pressure build-up.

16.25 Fire Fighting Agents

16.25.1 Types of fire fighting agent

The main types of fire fighting agent are (1) water, (2) foam, (3) vaporizing liquids, (4) dry powders, (5) inert gases and (6) other agents.

Accounts of fire fighting agents are given in the *Manual of Firemanship* (Home Office, 1974–) and by Guise and Zeratsky (1965, 1982), the Factory Mutual Engineering Corporation (FMEC) (1967), J.R. Hughes (1970), Hearfield (1970), Harpur (1971), the Petroleum Industry Training Board (PITB) (1975/6), Riley (1983), Fuchs (1984), Welker, Martinsen and Johnson (1986), and Scheinson, Penner-Hahn and Indritz (1989) as well as the various contributors to the NFPA *Handbook* referred to below.

The principal fire fighting agents are discussed in Sections 16.26–16.33.

16.25.2 Mechanism of fire extinguishment

Fire fighting agents have several different mechanisms of operation. These include:

(1) cooling of flame;
(2) reduction of fuel –
  (a) cooling of liquid,
  (b) dilution of liquid,
  (c) emulsification of liquid,
  (d) blanketing of liquid;
(3) reduction of oxygen;
(4) interference with combustion reaction.

The flame may be cooled to render it unstable. The supply of fuel to the flame may be reduced by cooling the liquid, by diluting or emulsifying it and so reducing the partial pressure of the vapour, or by blanketing the liquid with some inert material. The partial pressure of oxygen at the flame may be reduced by diluting the atmosphere with inert gas. The combustion reaction may be disrupted by the use of an agent which interferes with the combustion chain reaction.

16.25.3 Hazards of fire fighting agents

There are a number of hazards in the use of fire fighting agents. They are associated primarily with (1) discharge of the agent, (2) incompatibility between the agent and the material on fire, (3) an electric shock from high voltage equipment and (4) toxic and asphyxiant effects from the agent or its breakdown products.

A treatment of the toxic and asphyxiant hazards is given in GS 16 *Gaseous Fire Extinguishing Systems: Precautions for Toxic and Asphyxiating Hazards* (HSE, 1994). This deals with the hazards associated with systems using inert gases such as carbon dioxide and nitrogen and those using vaporizing liquids such as halons.

These hazards and the precautions to be take against them are considered in more detail in the following sections. Further discussion of the precautions advised in GS 16 is deferred to Sections 16.30 and 16.31 so that an account can first be given of the basic methods.

16.25.4 Methods of delivery

The principal methods of delivery of fire fighting agents are, in broad terms, (1) fixed systems, (2) mobile systems and (3) portable systems. Fixed systems encompass both fixed systems consisting of nozzles and feeder pipework and fixed monitors. The following sections give a more detailed discussion of these different types of delivery system.

16.25.5 Application of agents

For fire extinguishment or control agents such as water, foam and dry chemicals are generally applied directly to the burning liquid surface, and fixed systems are arranged to do this.

For agents such as dry chemicals, inert gases and vaporizing liquids, two widely used fixed systems are:

(1) total flooding system;
(2) local application system.

A manual method applicable to the first two of these is the use of a

(3) hand held hose line.

A total flooding system is used to protect a space which is essentially enclosed, whilst a local application system is used for a particular hazard such as an open tank. A hand held hose line is used to direct a jet of the agent at the fire.

Medium and high expansion foams may also be used in total flooding and local application systems.

16.25.6 Compatibility of agents

The compatibility of fire fighting agents has two distinct aspects: (1) compatibility with the material and/or a fire of the material and (2) compatibility with other agents.

Some fire fighting agents are incompatible with some chemicals. Information on this aspect is given in *Dangerous Substances. Guidance on Dealing with Fires and Spillages* (Home Office, 1972/4), in *Hazardous Loads* (IFE, 1972), *Fire Protection Guide to Hazardous Materials* (NFPA, 1991/27) and by various authors in the NFPA *Handbook*, as described below.

The most widely used fire fighting agent is water, but it is not suitable in all cases. For example, water reacts with aluminium alkyls, usually with some violence. In some cases the incompatibility is with the fire of the material rather than with the material as such. For example, water is not incompatible with bulk titanium, but it is unsuitable for a titanium fire. Water is not generally an appropriate agent for fires of alkali metals, sodium chlorate or sodium peroxide. Chemicals which are incompatible with water may generally be expected to be incompatible with water-based foam, particularly the low expansion variety.

It is important that full information is available on the proper agents for fighting fires with the chemicals used in the process, that the right agents are selected and are available on the plant, and that personnel understand the nature of the agents and their use.

The other type of incompatibility is that exhibited between two different agents. It is often desirable to use two agents, either together or in quick succession. An example is the use of dry chemicals to knock down a fire and then of foam to blanket the liquid and prevent reignition. In such applications the agents must be compatible. This aspect is discussed further below in relation to specific agents. Examples of work on the compatibility of foams and dry chemicals are the accounts by Hird and Fippes (1960), the Underwriters Laboratories (1963) and Jensen (1964).

16.25.7 Selection of agents

In fire fighting there is no single aim, and the selection of fire fighting agents reflects this. An agent may be required to effect (1) extinguishment, (2) control or (3) exposure protection.

For fire extinguishment or control, the first consideration is usually given to water. Water is cheap and generally readily available. It is non-toxic and does not give rise in fire to toxic products. It has a large capacity to absorb heat, whether as sensible or latent heat. It vaporizes to give some 1700 times its own volume of steam, which acts as an inert vapour. Water is therefore particularly useful in fires where high cooling capacity is needed such as those involving solid materials and high flashpoint liquids, and where it is necessary to cool hot metal to prevent flashback.

There are some disadvantages, however, in the use of water. Since water has a higher density than most flammable liquids, it does not generally float on the surface of a burning liquid and so blanket it. Instead it often displaces the liquid from any depression, bund or equipment containing it and may thus cause burning liquid to spread out.

Its effectiveness against liquid fires depends on the type of liquid. This is discussed in more detail below. It is sufficient to note here that with some liquids water is not a very efficient extinguishant.

There are some liquids where the use of water can be positively hazardous. This may be the case where there is an undesirable reaction between the liquid and the water so that an explosive or toxic hazard is created. This aspect has been discussed above.

Where the liquid is a refrigerated liquefied gas, the use of water for fire fighting is generally discouraged except for very small fires, since it has the effect of

increasing the vaporization of the liquid. Further discussions of the use of water with LNG and with LFG fires are given in Section 16.35.

Water conducts electricity in the solid stream condition and water jets should not be used against electrical fires. This aspect is discussed further in Section 16.34.

Water is a relatively ineffective agent on a weight basis and is not very attractive for self-contained mobile, and particularly portable, equipment. This characteristic is less significant for use in fixed systems, where the quantities used are large.

Fire extinguishment by blanketing may be achieved using foam. Foam is frequently the most effective agent for fire on liquids in spillages, bunds and storage tanks. Foam is essentially expanded water and, apart from its density, has the general characteristics of water. It is just as unsuitable as water for fighting fires involving electrical equipment or substances which have undesirable reactions with water. The uses and limitations of foam are considered in Section 16.28. There are a number of different types of foam, each with its characteristic uses.

The other principal agents are dry chemicals, vaporizing liquids and inert gases. Their uses and limitations are treated below.

It should be appreciated that where use is made of agents which are available in limited amounts only, it is essential to kill the whole fire first time. The supply of dry chemicals, for example, is usually sufficient to last only some tens of seconds. Unless the fire is completely extinguished, it is likely to reignite. On the other hand, foam forms a relatively long-lived blanket on the liquid and thus prevents re-ignition. This ability to hinder re-ignition makes foam an especially useful fire fighting agent.

It is necessary to establish that the fire fighting agent selected is capable of extinguishing a fire on the particular chemical concerned and this may require that tests be conducted. As already mentioned, tests may be needed to check the effectiveness of foam; they may also be necessary to verify that of vaporizing liquids or dry powders.

In selecting a fire fighting agent, regard should be given to hazards to personnel. This aspect of selection is discussed in GS 16.

16.26 Fire Protection Using Water: Extinguishment and Control

Water is used in several distinct ways to fight fire. These are:

(1) extinguishment of fire;
(2) control of fire;
(3) fire exposure protection;
(4) fire and explosion prevention.

The third application is discussed in the next section and the others in this section.

Fire protection using water is treated in the NFPA *Handbook* by Hodnett (1986e). Two principal codes are NFPA 13: 1991 *Installation of Sprinkler Systems* and NFPA 15: 1990 *Water Spray Fixed Systems*.

16.26.1 Water as a fire fighting agent

Some general characteristics of water as a fire fighting agent have been outlined in the previous section. Further aspects are considered here, particularly in relation to fires of flammable liquids.

Water is much the most widely used fire fighting agent. The majority of fires which occur are fires in buildings or fires of other solid materials, and for these the most suitable agent is generally water. But water is also important as an agent for fighting fires, including liquid fires, in process plant.

It is most effective against fires of high flashpoint liquids. The principal mechanism is the cooling of the liquid so that its vaporization is reduced. The cooling effect is strong, because water has a high latent heat. With fires of low flashpoint liquids, however, it becomes more difficult using water to achieve a sufficient reduction in the vaporization.

Another important mechanism by which water extinguishes liquid fires is vaporization to form steam, which blankets the fire and cuts off the oxygen.

In fires of particular liquids other mechanisms may be involved. If the liquid is miscible with water (e.g. ethylene oxide), addition of water reduces the vapour concentration. A similar result is obtained if the water added forms an emulsion on the surface of the liquid. If the liquid is denser than water (e.g. carbon disulphide), water floats on the surface and prevents vaporization altogether.

On the other hand, if the liquid has a low boiling point, and particularly if it is a refrigerated liquefied gas, the effect of adding water is not to take heat away from the liquid as latent heat of vaporization of water, but to put heat in as sensible heat of cooling of water, and thus to increase the vaporization of the liquid.

The water used to fight a fire may be large in volume and is liable to become contaminated. Its removal can pose a serious problem. This may well be a factor in the deciding whether water is the appropriate agent to use.

The hazards associated with the use of water for certain types of fire are discussed in Section 16.26.3.

16.26.2 Extinguishment of liquid fires

Work has been done by Rasbash and co-workers on the extinction of liquid fires (e.g. Rasbash and Rogowski, 1957; Rasbash and Stark, 1960, 1962; Rasbash, Rogowski and Stark, 1960; Rasbash, 1962). The work has been reviewed in relation to water spray systems by P. Nash (1974b). For this purpose flammable liquids may be divided into three classes, depending on the mechanism of extinction:

(1) liquids not miscible with water and with a fire point $> 45^{\circ}C$;
(2) liquids miscible with water and therefore capable of having their fire point raised above $45^{\circ}C$ by the addition of water;
(3) liquids not miscible with water and with a fire point $< 45^{\circ}C$.

The first class of liquid may be extinguished by heat transfer from it to water drops which penetrate its surface until its temperature falls below the fire point. Such liquids include heavy fuel oil, diesel oil, gas oil, and, as a borderline case, kerosene.

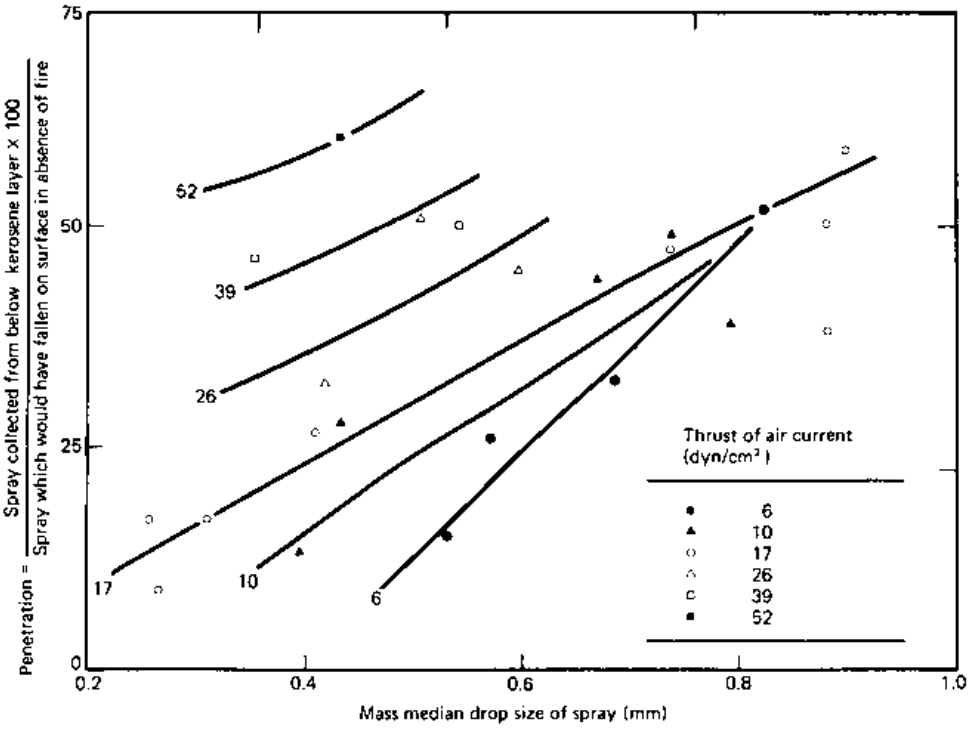


Figure 16.126 *Effect of the mass median drop size on the penetration of a water spray into a flammable liquid surface (Rasbash, 1962): kerosene fire, 30 cm diameter; downward application of spray; pressure at spray nozzle 0.35–2.1 bar (5–30 lbf/in.^{2}); flow rate to fuel surface in absence of fire 0.4–1.2 g/cm^2 min (Courtesy of the National Academy of Sciences)*

The water drops must enter the liquid in sufficient quantity despite the updraught of the flames and the evaporation of the spray in the flames. Factors which assist in achieving this are positioning of the spray near the liquid surface, high spray impetus and large liquid drop size. The impetus of the spray depends on the reaction of the nozzle and the width of the spray.

Figure 16.126 shows the results of some experiments of kerosene burning in a 30 cm diameter vessel with downward application of the spray (Rasbash, 1962). The ratio of the water actually penetrating the liquid surface to that expected to do so from geometrical considerations varied from about 10% to about 60%, depending on the thrust of the air current and the drop size of the spray. It was found that a mass median drop size above 0.4 mm is necessary to penetrate the flames effectively, but that at a drop size of about 0.8 mm the penetration becomes nearly independent of impetus and that above this size there begins to be a problem with splash fires caused by the larger drops splashing liquid from the surface so that burning continues even after the average liquid temperature has fallen below the fire point.

The work demonstrated that extinction can be achieved by application of water above a critical rate which is given by the equation

$$R_c = k_1 \frac{D^{n_1}}{\Delta T^{n_2}} \qquad [16.26.1]$$

where D is the mass median drop size (mm), R_c is the critical rate of water application (l/min), ΔT is the difference between the water temperature and the liquid fire point (°C), k_1 is a constant, and n_1 and n_2 are indices.

In practice it is necessary for the value of ΔT to be at least 40°C if the critical rate is not to be excessive. The indices n_1 and n_2 are approximately unity. The constant k_1 is a function of the flammable liquid, the area of the fire and the time for which the fire has already been burning. For a tray of gas oil of 8 ft diameter which had burned for 5 minutes before spray application, the value of k_1 was approximately 1140.

The time taken to extinguish the fire at rates of water application above the critical value is given by the equation

$$t = 5.2 \times 10^5 \frac{D^{0.85}}{R^{0.67} \Delta T^{1.67}} \qquad [16.26.2]$$

where R is the rate of water application ($l/m^2 s$) and t is the time to extinguish the fire (s).

Water spray systems for this liquid class typically use rates of water application in the range 0.16–1.2 $l/m^2 s$ (9.6–72 $l/m^2 min$). High velocity nozzles are used with nozzle pressures of 2.75 bar (40 psig) or above and with a conical spray. The desirable mass median drop size is an even distribution in the range 0.4–0.8 mm and the drops should have a velocity sufficient to penetrate the liquid surface.

When a deep pool of liquid in this class is burning, it may form after a period a 'hot zone' and water below the surface may then boil and cause a 'slopover', thus spreading the fire. This can happen, for example, with fuel oil which has been burning in depth for 15–30 min. It is necessary, therefore, to try to detect and extinguish fires before a hot zone occurs.

The second class of liquid may be extinguished by diluting the surface layer with water until the fire point of the mixture is raised sufficiently to cause extinction. Typical liquids are ethanol and acetone.

Although in this case the basic requirement for extinction is rather simple, there are certain problems. It is not always easy to tell when extinction has been achieved, since flames may continue to burn at some point and may be difficult to detect due to their low luminosity. Even if the fire is extinguished, the liquid remains flammable unless the whole bulk is diluted, and this may not be easy to achieve without spreading the spillage. Acetone, for example, requires a dilution of some 30 : 1.

The mass median drop size for a water spray for this liquid class should be less than 0.4 mm.

Liquids which are only partially miscible with water and have a low fire point are difficult to extinguish with water and generally their fires can only be controlled. Such liquids include ether and methyl ethyl ketone.

For water spray systems for such partially miscible liquids rates of water application in the range 0.12–0.30 $l/m^2 s$ (7.2–18 $l/m^2 min$) are normally required with nozzle pressures of 1.4 bar (20 psig) or above.

The third class of liquid may be extinguished by cooling the flame by heat transfer to the water droplets falling through it. Such liquids include petrol and, again as a borderline case, kerosene. It has been estimated that to cool a kerosene flame to extinction it is necessary to remove about 0.1 $cal/cm^3 s$ if extinction is solely by steam formation and about 0.7 $cal/cm^3 s$ if it is entirely by cooling. Thus the rate of heat removal to achieve extinction is of the order of 0.1–1 $cal/cm^3 s$, depending on the conditions.

The drop size required depends on several factors. In general, the extinction time falls sharply as drop size is reduced. With some liquids such as petrol it is essential that the drops penetrate to the lower part of the flames. There can be some 'sputtering' at the liquid surface, however, in the early stages of extinction if the drop size is too small. A mass median drop size of about 0.3 mm is usually suitable. Medium velocity nozzles of the open or closed type are used.

Additional cooling is obtained from air entrained with the spray. This effect is increased by the use of high nozzle pressures and drop velocities.

Water sprays are also used to deal with certain electrical fires, as described in Section 16.34.

16.26.3 Hazards associated with water

Although water is the most common fire fighting agent, there are certain cases where it use is hazardous. One such case is where the material is incompatible with water, as discussed in the previous section. Another is where the fire is incompatible with water. This applies to in particular to metal fires, which are considered in Section 16.34.

The use of water on live electrical equipment involves the hazard of electrical shock. The extent to which water can be used with electrical fires is discussed in Section 16.34. Also, as already mentioned, the use of water in large quantities and contamination of this water can pose a problem of disposal. Uncontrolled release of such water can cause damage to the environment.

16.26.4 Delivery systems for water

Water is delivered to the fire mainly either by fixed systems such as water sprinkler and water spray systems and fixed water monitors or by mobile systems such as fire hoses. Little use is made of water in portable systems.

Fixed water systems are used both indoors and outdoors. Indoors, widespread use is made of water sprinkler systems. Water spray systems may also be used indoors. Outside water spray systems and fixed water monitors predominate.

16.26.5 Applications of fire extinguishment or control

For most fire protection applications water is the agent of choice.

Fixed water sprinkler systems are used to protect indoor areas. Fixed water spray systems are used indoors to protect specific equipment such as grinding mills or conveyors.

Outdoors, fixed water spray systems are used to protect vulnerable items, loading and unloading facilities, including jetties, and storage vessels. Fixed water monitors are also provided for tank farms and jetties.

Except where it is unsuitable, water is the main agent used in mobile equipment by the works and public fire services for fighting fire wherever it occurs.

16.26.6 Fixed water sprinkler systems

Fixed water delivery systems are widely used in process occupancies. Fixed water sprinkler systems are used for fire extinguishment by delivering specified quantities of water over the protected area, mainly in buildings and warehouses. Fixed water spray systems are used for fire extinguishment or control by delivering specified quantities of water spray, characterized by the nozzle used, onto the protected equipment or area.

There is a considerable literature on fixed water sprinklers systems. It includes treatments by O'Dogherty, Nash and Young (1966), the Fire Offices Committee (1968), Kalelkar (1971), P. Nash (1972a, 1973a, 1976, 1975a,b, 1975 BRE CP 79/75, 1977a,b, 1990), Leworthy (1975), Nash, Bridge and Young (1974 BRE CP68/74), Nash and Young (1975 BRE CP29/75, CP67/75, CP 52/76, CP77/75, CP78/75), Rogers (1977 BRE CP9/77), Nicholls (1981), R. Young (1981), Theobald (1987a,b), Yao (1988), FMRC (1991) and Melinek (1993b).

Fire protection by fixed water sprinkler systems is treated in the NFPA *Handbook* by several authors,

notably Hodnett who deals with automatic sprinklers (1986a), automatic sprinkler systems (1986b) and water supplies for sprinkler systems (1986d).

Relevant NFPA codes are NFPA 13: 1991 *Installation of Sprinkler Systems*, NFPA 13A: 1987 *Inspection, Testing and Maintenance of Sprinkler Systems*, NFPA 16: 1991 *Deluge Foam–Water Sprinkler and Spray Systems* and NFPA: 16A: 1988 *Installation of Closed-Head Foam–Water Sprinkler Systems*. Other NFPA publications on sprinklers include *Automatic Sprinkler and Standpipe Systems* (1990/25), *Automatic Sprinkler Systems Handbook* (1994/37) and *Installation of Sprinkler Systems* (1994/39). The relevant British Standard is BS 5306 *Fire Extinguishing Installations and Equipment on Premises*, Part 2: 1990 *Specification for Sprinkler Systems*.

NFPA 13 is a large code, covering the use of sprinklers generally rather than in the process industries.

The elements of a fixed water sprinkler system include the sprinkler alarms, the sprinkler heads, the water distribution pipework, the valves and other fittings, and the water supply system and disposal arrangements.

The NFPA gives a classification of occupancies relevant to sprinkler systems. Those with moderate or substantial amounts of flammable liquid fall into the group Extra Hazard (Group 2).

A sprinkler system needs to respond rapidly so that the fire is extinguished before it can take hold. The time response of the sprinkler head is therefore crucial. Traditionally sprinkler heads have been classed according to the temperature at which they respond (e.g. 68°C). For fast response it is the time constant which matters. Fast response sprinklers are discussed by P. Nash (1972a), Watson (1984), Field (1985), Murrell (1988) and Mullhaupt (1986).

The use of sprinkler systems as fire sensors is considered by Nash and Theobald (1976 BRE CP50/76).

A sprinkler system needs to be designed so that each head is supplied with the intended water pressure. The hydraulics of sprinklers are treated in *Hydraulics of Fire Protection Systems* (FMEC, 1977) and *Sprinkler Hydraulics* (Wass, 1983) and by Nickerson (1954), C.M. Wood (1961), Beyler (1977), Ashfield (1979), Barris and Conte-Russian (1980), Bray (1980), Cresswell (1980), Kitson and Guy (1980) and Crowley (1982).

One way of achieving a uniform distribution of water in a sprinkler system is the use of a balanced system in which this uniformity is assured by the similarity of the pipework from the source to the individual sprinkler heads. For a system which it not balanced in this way it is necessary to ensure uniform distribution by calculating the pressure drops between the source and the individual heads.

16.26.7 Fixed water spray systems

As just indicated, fixed water spray systems are distinguished by the fact that the spray is characteristic of the type of nozzle used.

Accounts of fixed water spray system are given by Rasbash and co-workers, as already described, and by P. Nash (1974b), Hems (1979, 1983), Fritz and Jack (1983), Angelini (1984), Lev and Strachan (1989a,b), McCaffrey (1989), Chow and Fong (1991) and Jackman and Nolan (1994).

Fire protection by fixed water spray systems is treated in the NFPA *Handbook* by Hodnett (1986c).

Relevant codes and standards are NFPA 15: 1990 *Water Spray Fixed Systems* and NFPA 16: 1991 *Deluge Foam–Water Sprinkler and Spray Systems*.

The elements of a fixed water spray system include the fire detection and alarm system, the spray nozzles, the water distribution pipework, the valves and other fittings, and the water supply system and disposal arrangements.

16.26.8 Fixed water monitors

For fire risks involving large quantities of flammable liquid, notably tank farms and jetties, fixed water monitors are generally provided. These monitors are generally dual purpose devices which can be used to project water or foam.

16.26.9 Water rates for extinguishment or control

Recommended water rates for the extinguishment or control of fire are given in the various codes and standards. Those recommended by the NFPA probably have the greatest currency. NPFA 15 distinguishes the four types of application, listed at the beginning of this section, and gives for each type a recommended approach.

NFPA water rates for fire extinguishment

For fire extinguishment, NFPA 15 states that water rates should be based on tests or experience. It gives a general, or default, range of water rates which applies to the protected surface for most combustible solids and flammable liquids. This is 0.2–0.5 USgal/ft^2 min (8.1–20.4 l/m^2 min).

NFPA water rates for control of burning

For control of burning, NFPA 15 states that the water rate on the probable surface of the spill should not be less than 0.5 USgal/ft^2 min (20.4 l/m^2 min).

Control rather than extinguishment of the fire implies that the water flow needs to be maintained. NFPA 15 requires that the system function at full effectiveness until there has been time for the flammable material to be consumed, for the leak to be shut off, for the assembly of repair forces, etc.

NFPA water rates for exposure protection

For exposure protection, or cooling, the water rates recommended in NFPA 15 vary according to the item protected. They are considered in the next section.

NFPA water rates for fire and explosion prevention

For fire and explosion protection NFPA 15 simply states that the water rate should be based on tests or experience.

Critique of NFPA recommended water rates

A critique of water rates traditionally recommended has been given by Fritz and Jack (1983). They take as their starting point the then current edition of NFPA 15 and deal both with water rates for extinguishment or cooling and rates for exposure protection.

They refer in particular to work at the Rubber Reserve Company in the 1940s on horizontal cylindrical vessels

containing fuel (gasoline, butane and butadiene–butylene mixtures) and engulfed in fire.

Fritz and Jack discuss the work of Rasbash and co-workers on fire extinguishment described above. They draw attention to the influence of the water nozzle and spray characteristics on the water rates needed for extinguishment and to the fact that these characteristics are not specified in the NFPA codes. They consider the water rate required to effect extinguishment based on a heat balance model in which the total heat released by combustion goes to evaporate the water. They obtain from this a water rate of 2.5 USgal/ft^2 min. On this basis they suggest that a water rate of 0.5 USgal/ft^{2}min is no more than cosmetic. They also discuss the water rate for exposure protection, as discussed in the next section.

16.26.10 Fire water supply systems

The amount of water needed for the fighting and cooling presents a considerable problem. Aspects where better understanding may lead to less onerous requirements include the heat flux from liquid fires, the reflectivity and wetability of tank surfaces, and methods of applying the water to the surfaces.

Water spray systems both for fire fighting and for cooling may be of two types. In a wet system the pipes are kept full of water under pressure, whereas in a dry system these pipes are normally empty and are filled by the opening of a master valve only when the system is to be activated. A dry system should be used where there is risk of freezing. It is therefore this type of system which is most suitable for process plants, particularly in the open. The pipework in a dry system needs to be arranged to allow complete drainage.

There should be a secure water supply to the water spray system. This aspect is discussed in Chapter 10 in relation to plant layout.

There are a number of ways in which a water spray system can be rendered ineffective. One of these is freezing up, as just mentioned. Another is leaving valves closed, particularly after maintenance. The latter occurrence needs to be guarded against by specific procedures.

In addition, it is not uncommon for a water spray system to be knocked out by an explosion. The Fourth Edition of the Dow *Guide* (Dow Chemical Company, 1976) states that where an explosion hazard exists, it is a recommended minimum prevention and protection feature that water spray piping of $2\frac{1}{2}$ in. diameter or above be welded or flanged, not threaded.

16.26.11 Fire water disposal systems

As already indicated, the disposal of fire water, particularly contaminated water, can be a serious problem, which it is sufficient here to highlight. As an aspect of plant layout, fire water disposal is treated in Chapter 10. A method of alleviating this problem which merits mention here, however, is the use of foam to obtain a given degree of fire extinguishment or control with a smaller water usage.

16.27 Fire Protection Using Water: Exposure Protection

In the foregoing section an account has been given of the use of water to extinguish or control a fire. In this section consideration is given to its use for exposure protection by cooling of equipment exposed to fire.

Accounts of fire exposure protection are given by Pettit (1945), Chaillot (1966), P. Nash (1973b, 1974a), Fritz and Jack (1983), Billinge, Moodie and Beckett (1986), Lev and Strachan (1989b), Lev (1991) and Meiers and Jarman (1993).

As indicated above, a relevant code for exposure protection using water is NFPA 15.

16.27.1 Delivery systems for water

The means of delivery of water for cooling are broadly similar to those used for extinguishment. Water is delivered to the protected surface by fixed systems such as fixed water spray systems and fixed water monitors or by mobile systems such as fire hoses.

16.27.2 Applications of water cooling

Essentially, exposure protection is provided for large flammable gas or liquid inventories which are liable to be exposed to a fire. For the most part such inventories occur in storage tanks and vessels, though protection may also be provided for certain process vessels and for road and rail tankers.

The purpose of providing such protection is to cool the metal and so prevent loss of strength. It is normal to provide the tank or vessel with pressure relief but, even if the relief operates, it will not prevent failure if the wall temperature is allowed to rise too high.

16.27.3 Water rates for cooling

NFPA water rates for cooling

For exposure protection by cooling, NFPA 15 treats the following cases: vessels, structures and miscellaneous equipment, transformers and belt conveyors.

For vessels, the code states that the rules given assume that there is a relieving capacity based on a maximum allowable heat input of 6000 BTU/ft^2 h (18.9 kW/m^2). If there is no such relief, the water rates should be increased accordingly.

For a vertical or inclined vessel surface the water rate should not be less than 0.25 USgal/ft^2 min (10.2 l/m^2 min) of exposed uninsulated surface. Where on such a surface rundown is assumed, the vertical distance between nozzles should not exceed 12 ft (3.7 m). The horizontal extremities of the spray patterns should at least meet.

For a vertical vessel the bottom and top surfaces should be completely covered by directed water sprays with a water rate of 0.25 USgal/ft^2 min (10.2 l/m^2 min) of exposed uninsulated surface. On the bottom surface the horizontal extremities of the spray patterns should at least meet.

The surfaces below the equator of a spherical or horizontal cylindrical vessel cannot be considered to be wetted by rundown.

The code also gives various other provisions.

The structures and equipment considered are primarily horizontal and vertical structural steel members, pipework and pipe racks, and cable trays and cable runs. Water rates are given for each of these.

Critique of NFPA recommended water rates

Mention has already been made of the critique by Fritz and Jack (1983) of the water rates recommended in NFPA 15 for fire extinguishment or control. These authors also review the NFPA recommendations on water rates for exposure protection.

The background to these recommended rates is work on heat fluxes to vessels engulfed in fire, such as the tests listed in API RP 520: 1990 and earlier editions, which include the Rubber Reserve Company tests mentioned in the previous section.

In this case the authors base their estimate of the cooling water requirement on a heat removal rate of 20 000 BTU/ft^2 h, effected by a rise in water temperature to a few degrees above the boiling point. On this basis they obtain an estimate of 0.04 USgal/ft^2 h for the required water rate. They suggest that the NFPA recommended value of 0.25 USgal/ft^2 h is higher than it need be.

Thus Fritz and Jack's critique of the NFPA water rates recommended is that for fire extinguishment they are too low, but that for exposure protection they are too high.

Other recommended water rates

For the exposure protection of storage tanks containing low fire point liquids a rate of water application over the surface of the tank of 0.2 UKgal/ft^2 min (0.16 l/m^2 s) is recommended by P.H. Thomas and Law (1965 FRS Fire Res. Note 609).

The Fourth Edition of the Dow *Guide* (Dow Chemical Company, 1976) gives as a recommended minimum fire prevention and protection feature exposure protection a rate of 0.20–0.35 USgal/ft^2 min (0.14–0.24 l/m^2 s) for directional sprays. The later editions give water rates as part of the loss control credits, but these refer to indoor sprinkler applications.

For the exposure protection of LFG vessels the ICI *LFG Code* (ICI/RoSPA 1970 IS/74) recommends a rate of 0.20 UKgal/ft^2 min (0.16 l/m^2 s), but allows a reduced rate if certain precautions are taken. This is discussed more fully in Chapter 22.

16.27.4 Cooling of tank exposed to a pool fire

A tank exposed to fire, including an engulfing fire, may be cooled by applying water. The water rates recommended have just been described. At these water rates the total water requirements may be very large. The requirements for exposure protection generally greatly exceed those for extinction of fire.

This generalized requirement is not difficult to meet for small tanks, but becomes much more onerous for large ones. Thus, based on this criterion, the water requirement for an 80 m diameter tank is of the order of 150 t/min. The power required to lift and distribute the water is large also, being about 1 MW.

The water needed for exposure protection is greatly reduced if application is restricted to the tank roof and ullage sections. Figure 16.127, given by P. Nash (1973b, 1974a), illustrates this difference. The curves are based on the water rates recommended in the then current edition of NPFA 15, which were 0.25 USgal/ft^2 min. Curves A1 and B1 give, respectively, the water requirements for extinction and exposure with coverage of the whole tank and with coverage of the roof and ullage sections only. Curves A2 and B2 give the corresponding water requirements for exposure only.

A further discussion of the use of water sprays for protection against fire exposure is given in relation to storage in Chapter 22.

16.27.5 Cooling of vessel exposed to an impinging jet flame

A rather different, and stringent, fire protection requirement arises where a jet flame impinges directly on a target. This problem has been studied by Lev and Strachan (1989b) and Lev (1991).

The surface of a vessel exposed to a jet flame is likely to rise to a temperature of over 100°C very rapidly. A continuous film of water over the metal surface is capable of intercepting radiant heat, but as the heat flux is increased the protection so afforded is gradually lost as the water film thins and then disintegrates.

A model for a water spray system to protect against jet flames has been described by Lev (1991). It has three main elements which model: (1) the three-dimensional droplet trajectory, (2) the in-flight evaporation loss and (3) the heat transfer between the cooling water and the metal surface.

For the droplet trajectory, the equation of motion of a droplet moving through a parallel gas stream is written as

$$m_d \frac{dv}{dt} = C_d \rho_g (U - v)(|U - v|) \frac{A}{8} - m_d g \qquad [16.27.1]$$

where A is the surface area of the droplet (m^2), C_d is the drag coefficient, g is the acceleration due to gravity (m/s^2), m_d is the mass of the droplet (kg), t is the time (s), U is the gas velocity (m/s), v is the droplet velocity (m/s) and ρ_g is the gas density (kg/m^3).

The drag coefficient is taken as given by the following relations for a non-evaporating droplet, the correction for evaporation being small:

$$C_d = 24/\mathrm{Re} \qquad \mathrm{Re} \leq 2 \qquad \text{Stokes regime} \qquad [16.27.2]$$

$$C_d = 10/(\mathrm{Re})^{\frac{1}{2}} \qquad 2 < \mathrm{Re} < 500 \qquad \text{Intermediate regime} \qquad [16.27.3]$$

$$C_d = 0.44 \qquad \mathrm{Re} \geq 500 \qquad \text{Newton's regime} \qquad [16.27.4]$$

with

$$\mathrm{Re} = \frac{D(|U - v|)}{\nu} \qquad [16.27.5]$$

where D is the droplet diameter (m) and ν is the gas kinematic viscosity (m^2/s).

For the in-flight evaporation loss, use is made of the correlation of Ranz and Marshall (1952), with the correction for high stream temperatures given by Yuen and Chen (1978):

$$\mathrm{Nu}(1 + B) = 2 + 0.6\mathrm{Re}^{0.5}\mathrm{Pr}^{0.33} \qquad [16.27.6]$$

with

$$B = (h_s - h_d)/L \qquad [16.27.7]$$

where B is a mass transfer number, h_d is the surface enthalpy of the droplet (J/kg), h_s is the free stream enthalpy (J/kg) and L is the latent heat of evaporation of

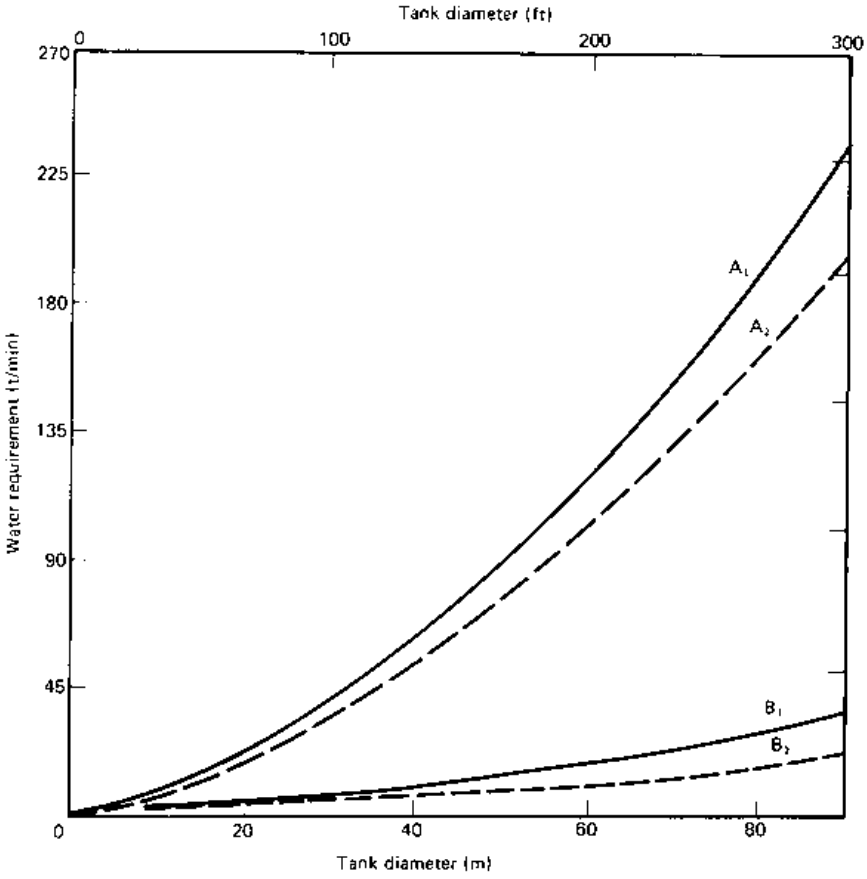


Figure 16.127 *Water requirements for protection against exposure to fire and for extinction of fire for a storage tank (P. Nash, 1974a): A_1, NFPA 15 – extinction and exposure; A_2, NFPA 15 – exposure only; B_1, 'economical' requirement – extinction and exposure; B_2, 'economical' requirement – exposure only (Reproduced by permission of HM Stationery Office. Copyright. All rights reserved)*

the droplet (J/kg). The properties are evaluated at the film temperature.

Since the work of Yuen and Chen was done using streams of hot air, it is necessary also to introduce a term for absorbed radiant heat:

$$M_r = cQA\,\delta t/L \qquad [16.27.8]$$

where c is an absorption coefficient, M_r is the rate of evaporation loss due to thermal radiation (kg/s), Q is the heat flux to the droplets (W/m^2) and δt is the time of exposure of the droplet (s).

For the heat transfer between the cooling water and the surface, the relation used is that of Yao and Choi (1987):

$$Q = 29.5 \times 10^{-4} G^{0.76} \qquad [16.27.9]$$

where G is the liquid mass flux (kg/m^2 s) and Q is the heat flux between the water and the surface (W/m^2).

Information on the flame temperature and surface emissive power in jet flames has been reviewed by Lev (1991). A study by Blything (1983 SRD R263) quotes a flame temperature of about 1300°C and heat fluxes of about 300–400 kW/m^2. Work on jet flames by Cowley and co-workers (Cowley, 1989; Tam and Cowley, 1989; Cowley and Pritchard 1991) on several different configurations has shown heat fluxes in the range 50–250 kW/m^2.

The model described was used to obtain results relevant to spray system design. These showed that the heat transfer passes through a marked maximum with surface temperature, this maximum occurring around 140–150°C. Thus the water mass flux to remove the heat from an incident heat flux of 250 kW/m^2 was 12 kg/m^2 min at 150°C but 50 kg/m^2 min at 300°C. Due to instabilities, maintenance of conditions where the lower water rate is sufficient is dubious. Lev recommends, therefore, a design cooling water rate of some 60–120 kg/m^2 min.

In order to deliver this cooling water under conditions where there is likely to be in-flight evaporation and crossflow losses, the droplets need to be large and to be projected at high velocity. Lev presents results from the

model showing the fraction of water droplets reaching the target as a function of crossflow velocity and droplet diameter. Droplets of less then 0.5 mm diameter are vulnerable and a droplet size of more than 1 mm diameter should be aimed for.

Typical medium velocity (MV) nozzles tend to produce a high proportion of droplets less than 0.5 mm in diameter. They appear less suitable than high velocity (HV) nozzles. Alternative modes of water delivery are hand-held monitors and fixed monitors. Suitable HV nozzles mounted less than 1 m from the target are capable of delivering the 60–120 kg/m^2 min required. There are hand-held monitors which from a distance of 16 m can deliver water at a rate of 120 kg/m^2 min, wetting an area of 6 m^2.

The method just described is applicable to impinging jet flames of LPG with stream temperatures of 500–1300°C and stream velocities up to 40 m/s with radiative heat fluxes of 50–250 kW/m^2 and for metal surface temperatures of 150–300°C.

16.27.6 Fixed water cooling systems

Exposure protection is effected using fixed water spray systems. Proper cooling requires that water be applied such that the whole surface protected is wetted by the water rate specified. The spray nozzles should be located so that the extremities of the spray pattern at least meet, and for wetting below a vessel equator reliance should not be placed on rundown. More detailed requirements have been given in the previous section. The relevant codes, notably NFPA 15, have been discussed in the previous section.

16.28 Fire Protection Using Foam

A prime alternative to water, particularly for large fires, is foam. Accounts of foam are given by Burgoyne (1949a), Burgoyne, Katan and Richardson (1949a), the American Chemical Society (ACS) (1956), Burgoyne and Steel (1962), Vervalin (1964b,d), Meldrum and Williams (1965), Ashill (1966b), G. Nash (1966), Hearfield (1970), Hird, Rodrigues and Smith (1970), Meldrum (1972, 1982), P. Nash (1973b), Corrie (1974,1975 BRE CP25/75), Nash and Young (1975 BRE CP42/75), Burford (1976), Gillespie and Dimaio (1977), Murphy (1981), Boughen (1983), J.L. Evans (1985, 1988), SKUM (1986), A.A. Briggs and Webb (1988), Tabar (1989), Waters (1990 LPB 91) and M. Clarke (1992). Fire protection using foam is treated in the NFPA *Handbook* by Lockwood (1986).

Relevant codes and standards are NFPA 11: 1988 *Low Expansion Foam and Combined Agent Systems*, NFPA 11A: 1988 *Medium and High Expansion Foam Systems*, NFPA 16: 1991 *Deluge Foam–Water Sprinkler and Spray Systems*, NFPA 16A: 1988 *Installations of Closed Head Foam–Water Sprinkler Systems*, NFPA 11C: 1990 *Mobile Foam Apparatus* and BS 5306: 1976– *Fire Extinguishing Installations and Equipment on Premises*, Part 6: Foam, Section 6.1: 1988 *Specification for Low Expansion Foams* and Section 6.2: 1989 *Specification for Medium and High Expansion Foams*.

16.28.1 Mechanisms of fire extinguishment

Foams are widely used against liquid fires. Initially the foam acts as a blanketing agent and then, as the water drains from the foam, as a cooling agent.

16.28.2 Types of foam

Foams are water based and come in several kinds. These include:

(1) chemical foam;
(2) protein-based mechanical foam –
  (a) standard, low expansion foam,
  (b) high expansion foam,
  (c) medium expansion foam;
(3) special foams –
  (a) fluorochemical foam,
  (b) fluoroprotein foam;
(4) detergent foam.

There is now a large family of foams of different types and applications. One broad distinction is made on the basis of the viscosity of the foam. The blanket formed by the more viscous type is resistant to rupture by flame, but the less viscous type flows more readily over a liquid surface. Other relevant properties of foams are their resistance to oil and alcohols.

Chemical foam

Chemical foam is produced by reacting aqueous solutions of sodium bicarbonate and aluminium sulphate in the presence of a foam stabilizer. The reaction generates carbon dioxide, which both forms foam and ejects the mixture from the apparatus. This type of foam may be regarded as obsolete, its use long having been almost entirely confined to mobile and portable equipment.

Protein, or mechanical, foam (P)

Mechanical foam is generated by mechanical aeration of aqueous solutions of certain chemicals, which usually have a protein base. One type is based, for example, on blood hydrolysed by caustic soda. Standard foam is made by introducing the foam compound into the water in the hose to give a 3–6% aqueous solution and then mixing the solution with air in an ejector nozzle to give an approximately 10:1 expansion. This type of foam is the most widely used both for fixed and mobile apparatus. Such standard low expansion foam is very cheap.

High expansion foam is generally similar to standard foam but has an approximately 1000:1 expansion. This type of foam contains little water so that it acts almost entirely by blanketing rather than by cooling. It is very light and is easily blown away, and is thus more suitable for fires in containers such as tanks or ships' holds than for those in open situations such as in a bund.

Medium expansion foam is again generally similar to standard foam, but has an approximately 100–150:1 expansion. This type of foam is also light, but is not so easily blown away as high expansion foam.

Both medium and high expansion foams have a good three-dimensional extinction capability and can be used against fires on piles of materials such as rubber.

A disadvantage of protein foams is that if the foam blanket is broken the liquid may re-ignite and burn back the blanket. Low expansion foam, however, has reasonably good heat and 'burnback' resistance.

Fluorochemical, or light water, foam
Agents have been developed to overcome this problem. One type is fluorochemical foam. This includes 'light water' foam, which contains a straight-chain fluorocarbon surface active agent. This has the effect that as the water drains from the foam it spreads in a thin film over the liquid and seals it. Even if the film is disturbed by agitation, it reforms rapidly. Light water foam behaves differently, however, on different liquids, and it is not universally effective. The cost of light water foam is high.

Fluoroprotein foam (FP)
Another agent which works in a similar manner is fluoroprotein foam, which contains a branched chain fluorocarbon. It is therefore a candidate where good burnback resistance is needed. It is less expensive and appears in many cases to be more effective than light water foam. Fluoroprotein foam is less prone to pick up oil particles when passed through oil. This 'fuel-shedding' property is useful in subsurface foam injection on storage tanks. This type of foam tends to have good compatibility with dry chemicals.

Synthetic detergent foam (S)
Synthetic detergent foam is generated by mechanical aeration of aqueous solutions containing 2–3% of detergent. This foam is less stable than protein-based foam. The most effective method of usage appears to be massive application in a knockout attack. Detergent foam has enjoyed some popularity, the attraction being that it is cheaper even than protein foam.

Aqueous film forming foam (AFFF)
AFFF has low viscosity and spreads easily over a liquid surface. It can be an effective agent against deep-seated fires. Another useful property of AFFF is that does not need elaborate foaming devices and can be utilized in many water sprinkler and spray systems.

Film forming fluoroprotein foam (FFFP)
FFFP foam is another type of foam which has low viscosity and good spreading properties and can be used in many water spray systems. FFFP foam tends to drain rapidly and is therefore less reliable in maintaining a foam blanket.

Alcohol resistant (AR) foam
Regular air foams do not perform well on liquids which are of the polar solvent type, notably alcohols. For these AR foams have been developed. The first generation of AR foams were not entirely satisfactory, but effective foams have been developed. One type of AR foam is polymeric alcohol resistant AFFF.

Low temperature foams
Foams have been developed for use at low ambient temperatures; one quoted temperature for such foams is −29°C. These foams come in both protein and AFFF types.

16.28.3 Properties of foam
A foam for fire fighting should possess certain general properties, which include (1) expansion, (2) cohesion, (3) stability, (4) fluidity, (5) fuel resistance and (6) heat resistance.

Clearly, the foam must have an appreciable expansion ratio, its bubbles must cohere together and form a blanket, it must retain its water and remain stable, it must flow freely over the liquid surface and around any obstacles, it must not pick up so much fuel that it is itself liable to burn and it must resist the heat of flames on the liquid. Foams for use on alcohols must also be alcohol resistant.

Three quantitative criteria for foam are (1) the expansion, (2) the fluidity and (3) the drainage time. Expansion is measured by the expansion ratio.

A measure of fluidity is the shear stress. A shear stress in the range 150–200 dyn/cm^2, measured on a torsional viscometer, is typical of a good foam.

The drainage of liquid out of the foam is usually expressed as the '25% drainage rate', which is the time in minutes for 25% of the total liquid content to drain away under standard conditions. For a good foam this drainage time is typically 2–5 minutes.

Foam can be affected by the quality of the water used. A study by Dimaio and Lange (1984) detected deleterious effects from contaminants such as corrosion inhibitors, anti-fouling agents, etc. In general, however, such effects were found to be much weaker if high application rates were used.

Compatibility with other fire fighting agents is another important property of foams. This aspect has been discussed above and is considered further below.

16.28.4 Tests for foam
There are a number of standard tests to evaluate the performance of foam in extinguishing fire. Standard tests include the Underwriters Laboratories and Det norske Veritas (DnV) tests and those specified in the MIL Specification MIL-F.24385, the draft ISO/DP 7203 and, in the UK, Defence Standards 42–21, 42–22 and 42–24 and BS 6535: Part 6: 1988–. Such tests are discussed by J.L. Evans (1988) who compares the performance of different foams in different tests.

Tests may be required to establish the effectiveness of a foam in a particular application. Details of the conduct of tests to select a foam for methylisobutyl ketone (MIBK) have been given by Corrie (1974).

16.28.5 Hazards associated with foam
Foam is water based and, to this extent, hazards associated with water apply to foam also. They include increased vaporization of low boiling liquids, reaction with incompatible materials and electric shock from live electrical equipment.

Another hazard is rupture of the foam blanket and burnback, which may put fire fighters at risk.

Hazard can arise from the use of a foam on a liquid at a temperature of 100°C or above. The formation of steam can cause a four-fold expansion of the foam with slopover of the burning liquid.

In the case of the medium and high expansion foams used to fill spaces, there is the hazard of asphyxiation.

16.28.6 Hazards associated with foam: static electricity
Another hazard is ignition of hydrocarbons in a storage tank roof by static electricity from foam injection, as described by Howells (1993 LPB 114). This author

describes several incidents in which ignition of volatile refined products in a floating roof storage tank appears to have been caused by foam injection. He suggests two possible modes of charge generation: (1) the settling of water droplets through the hydrocarbon liquid and (2) the streaming current of the foam mixture leaving the nozzle.

Using Equation 16.7.173, Howells obtains for the case of a tank filled to a depth of 3 m with the bottom earthed, an estimated liquid surface potential of 27 kV, a value which has been shown in work on road tankers to be hazardous. He suggests that an even higher potential may occur if the foam jet is applied directly to the liquid surface so that the concentration of foam in the fuel is orders of magnitude higher than that used in this calculation.

With regard to the second mechanism, aqueous foam has a high conductivity and any charge generated at the nozzle would be quickly dissipated back to the branch pipe or the tank walls. However, if charged foam enters the liquid the charge could be retained. The streaming current of foam is not readily calculable, so experimental work was undertaken. At the time of writing this work was inconclusive.

16.28.7 Delivery systems for foam

Foam is delivered to the fire by means essentially similar to those used for water. The means used are mainly fixed systems such as foam–water spray systems and fixed foam–water monitors or mobile foam–water systems such as fire hoses. Little use is made of foam in portable devices.

The delivery of foam involves three stages: (1) proportioning of the foam concentrate, (2) foam generation and (3) foam distribution. There are a number of methods for the proportioning of the foam concentrate.

The devices for the generation of the foam are incorporated in the devices used for its distribution, as just described. The basic method of generation is aspiration of air into the foam.

A detailed account of methods of proportioning and distribution is given by Lockwood (1986).

16.28.8 Applications of foam

Fire extinction by blanketing may be achieved using foam. Low expansion foam is mainly used to prevent, extinguish or control fires in storage tank tops and bunds and on spills.

Foam should be used only if it is compatible with the hazardous liquid. In particular, foam is essentially expanded water and, apart from its density, has the general characteristics of water. It is just as unsuitable as water for fighting fires involving electrical equipment or substances which have undesirable reactions with water.

Other conditions for the use of foam are that the liquid surface be horizontal and that the temperature of the liquid be not too high. The liquid temperature should be below the boiling point. If the liquid temperature is below the boiling point but above 100°C, water in the foam will turn to steam, which can result in a very large expansion of the foam.

There are optimum rates of application of foam. For low expansion foam with an expansion ratio of 8:1 an application rate of 0.1 USgal/ft^2 min will give 0.8 USgal/ft^2 min of foam. Foam application rates are discussed by Lockwood (1986). The foam should be applied gently.

Medium and high expansion foams are used to prevent, extinguish or control fire in spaces such as ships' holds. Application systems for these foams comprise both (1) total flooding systems and (2) local application systems.

16.28.9 Fixed foam systems

For low expansion foam, one type of fixed foam system is the foam–water deluge system. Another type of system is the foam–water monitor. Fixed foam systems are used for fire prevention, extinguishment and control in bunds or on spills.

Relevant codes are NFPA 11 for low expansion systems, NFPA 11A for medium and high expansion systems, NFPA 16 for deluge foam–water sprinkler and spray systems and NFPA 16A for closed head foam–water sprinkler systems.

The fighting of a major fire requires a very large quantity of foam. An example quoted by G. Nash (1966) is a requirement of 300 × 5 UKgal drums for a 30 minute foam attack on a single 150 ft diameter oil storage tank. The supply, and disposal, of such a large number of drums in an area congested with fire appliances and hoses constitutes a major problem. He describes the alternative of providing a piped supply of foam concentrate.

16.28.10 Fixed foam systems for storage tanks

A particularly important application of foam is the protection of storage tanks. A variety of systems are used. Accounts of foam systems for storage tanks are given by E.M. Evans and Whittle (1974), P. Nash and Whittle (1978), Lockwood (1986) and SKUM (1986). A relevant code is NFPA 11.

For fixed roof tanks some principal arrangements are foam chambers, internal tank distributors and subsurface foam injection. Foam chambers are installed at intervals on the outside near the top of the tank wall, providing an over-the-top foam generation (OFG). An alternative is internal distributors fitted inside the tank.

Application of foam at the top of the tank poses several problems. If the fire is initiated by an explosion, this may well also disable the foam system. The upward flow of air caused by the fire may interfere with the distribution of the foam. In a large tank the foam may not reach the centre.

Subsurface foam injection is designed to counter these difficulties. Foam is injected under pressure up through the liquid in the tank. Injection may be through the product pipe or a dedicated line. Mobile foam trucks may be used to provide the foam supply.

Floating roof tanks may be open top or closed. They have a good fire record so that foam systems are generally not required, with one exception. This is the need to cater for rim fires which can occur on either type. An open-type floating roof tank may be protected by a fixed foam system which pours foam into the annulus formed by the tank wall and a foam dam. A closed floating roof tank may be protected using a top injection system similar to those used in fixed roof tanks. Subsurface foam injection is not generally used for floating roof tanks since a tilted or sunken roof can cause poor foam distribution.

16.28.11 Mobile foam systems

Foam trucks are the principal mobile mode of delivery for foam. The trucks are typically purpose built twin agent trucks with a capability of delivering dry chemicals also.

Relevant codes are NFPA 1901 which covers basic water systems with a foam option, and NFPA 11C which covers foam trucks.

Foam trucks carry a supply of foam concentrate and delivery hoses and can be equipped with telescopic booms or articulated towers. They have low clearances to allow passage under pipe bridges. A combined agent truck might typically carry AFFF and dry chemical. Monitor capacities are of the order of 500–1000 USgal/min.

There are a variety of mobile devices that can be used to apply foam to the top of a storage tank which is on fire. They include mobile foam monitors and foam towers. There are a number of problems in using a foam monitor for this purpose, such as crosswinds and fire updrafts, and a significant proportion can be wasted. Lockwood advises making an allowance of 60% above the desired application rate to allow for such factors.

16.28.12 Vapour suppression by foam

Fire control and extinguishment is not the only use of foam. Another important application is the suppression of vaporization from toxic liquid spills. This use of foam is treated in ASTM-F-1129-88 *Standard Guide for Using Aqueous Foams to Control the Vapor Hazard from Immiscible Volatile Liquids*. Vapour suppression using foam is discussed in Chapters 15 and 18.

16.29 Fire Protection Using Dry Chemicals

An alternative to water or water-based foam is dry chemicals, or dry powders. Accounts of dry chemicals include those by T.G. Lee and Robertson (1960), Vervalin (1964e), Laffitte *et al.* (1965), Emmrich (1971), Wesson (1972), Woolhouse and Sayers (1973), Schweinfurth (1974), Stauffer (1975), MITI (1976) and Ewing *et al.* (1989a,b). Fire protection using dry chemicals is treated in the NFPA *Handbook* by Haessler (1986).

Relevant codes and standards are NFPA 17: 1990 *Dry Chemical Extinguishing Systems* and BS 6535: 1989– *Fire Extinguishing Media*, Part 3: 1989 *Specification for Powder*.

The use of dry chemicals has been developed particularly in Germany, where some large fixed and mobile systems have been used. Since with dry chemicals it is essential to apply enough agent to extinguish the fire outright, their use on large fires requires the availability of large quantities.

16.29.1 Mechanisms of fire extinguishment

The principal mechanism by which dry chemicals act against fire is to cause chain termination of the combustion reactions. There are several other less significant mechanisms. The bicarbonate chemicals release carbon dioxide in an endothermic reaction. To some extent the gas evolved blankets the liquid and the gas evolution reaction has a cooling effect, whilst the particle cloud reduces the heat transfer between the flame and the liquid surface.

Treatments of the inhibition mechanisms and general theory of dry chemicals are given by Laffitte *et al.* (1965), Laffitte and Bouchet (1959), Dewitte, Vrebosch and van Tiggelen (1964), Birchall (1970), Iya, Wohowitz and Kaskan (1975), McHale (1975), Spence and McHale (1975), Vanpee and Shirodkar (1979), Mitani (1981, 1982, 1983) and Mitani and Niioka (1982).

The combustion chain reactions are broken by adsorption on solid surfaces. Thus for a given material a large powder specific surface enhances the effectiveness. Haessler (1986) states that best results are obtained with a particle size range of 10–75 μm with a median size of 20–25 μm.

16.29.2 Types of dry chemical

Some basic dry chemicals are (1) sodium bicarbonate (standard dry chemical), (2) potassium bicarbonate, (3) potassium chloride, (4) urea potassium bicarbonate and (5) monoammonium phosphate. There are also the formulations (6) general purpose powder (ABC) and (7) Monnex powder.

Standard dry chemical consists principally (over 90%) of sodium bicarbonate with additives to improve fluidity, non-caking and water repellent characteristics. Potassium bicarbonate formulations, however, are also used and are about $1\frac{1}{2}$–2 times as effective as those with the sodium bicarbonate base.

General purpose powder is a mixture of ammonium dihydrogen phosphate, diammonium hydrogen phosphate and ammonium sulphate.

Monnex is a potassium alkali based material. The particles disintegrate in contact with the flames and thus give a greatly enhanced surface area. Its effectiveness is about 5–6 times that of standard dry chemical.

16.29.3 Properties of dry chemicals

Dry chemical formulations may be ranked in respect of their effectiveness in extinguishing fires according to their performance in tests. This performance is a function both of the chemical composition and the particle size.

Some types of dry chemical based on sodium or potassium bicarbonate are not compatible with foam. The dry chemical, and particularly the additives, tend to break down the foam bubbles. However, foam-compatible forms of dry chemical are also available.

In storage, dry chemicals are stable at normal and low temperatures but deteriorate at high temperature. Haessler quotes an upper temperature for storage of 120°C. Different dry chemicals should be segregated. Mixing of alkali and acid agents can result in release of carbon dioxide, and incidents have occurred where extinguishers have exploded.

16.29.4 Hazards associated with dry chemicals

One hazard from the use of dry chemicals is that due to the sudden release of the agent. Another hazard is unexpected reignition. The main toxic hazards following the use of dry chemicals will generally be those due to the combustion process. Dry chemicals themselves are non-toxic.

16.29.5 Delivery systems for dry chemicals

Dry chemicals are delivered to the fire mainly by fixed systems, from cylinders or by mobile systems. They are

also one of the agents used in portable extinguishers. Delivery from cylinders is by hand held hose line.

16.29.6 Applications of dry chemicals

Dry chemicals are used to extinguish fire. They are utilized on Class A fires (combustible materials), Class B fires (flammable liquids) and Class C fires (electrical equipment) in the NFPA classification. With regard to the latter, dry chemicals tend to be somewhat corrosive and to insulate contact surfaces. They are not suitable, therefore, for fires in delicate electrical equipment but can be used on fires of equipment such as transformers and circuit breakers.

Dry chemicals are an extremely versatile type of agent. They are low hazard and non-toxic. They can deal with a wide range of fires. They find application to extinguishment of large outdoor fires, to protection of spaces indoors and in portable extinguishers.

A dry chemical agent acts by extinguishing the fire in a single shot. In this is can be extremely effective. It is necessary, however, to use sufficient powder to ensure that the flame is completely extinguished. Otherwise once the powder is exhausted reignition is liable to occur. A dry chemical has little cooling effect and does not leave behind an inert atmosphere.

There are also other potential causes of reignition when a dry chemical is used. Vapours from a flammable liquid may be reignited by a hot surface, a combustible solid may be reignited by smouldering material and an electrical fire may reignite due to continued arcing.

If the fire is one in a combustible material and there is no reason why water should not be used, it may be advisable to use follow up with water to complete the extinguishment of the fire.

16.29.7 Fixed dry chemical systems

Fixed dry chemical systems may be (1) total flooding systems or (2) local application systems. A fixed system may be supplemented by hand held hose lines from cylinders.

16.30 Fire Protection Using Vaporizing Liquids

Another type of fire fighting agent is the vaporizing liquid. Accounts of vaporizing liquids include *Halogenated Fire Suppressants* (Gann, 1976) and those by Burgoyne and Richardson (1949a), Rasbash (1968), Hirst (1974a,b), Boughen (1979, 1982), Forrester (1982), Peissard (1982), Capper (1983), C.C. Grant (1985), Hoskins (1985), R.J. Martin, Shepherd and Hamlin (1986), Goodall (1988), Boyce (1990) and Senecal (1992a,b). Fire protection using vaporizing liquids is treated in the NFPA *Handbook* by D.W. Moore (1986).

Relevant codes and standards are NFPA 12A: 1992 *Halon 1301 Fire Extinguishing Systems*, NFPA 12B: 1990 *Halon 1211 Fire Extinguishing Systems*, NFPA 2001: *Clean Agent Fire Extinguishing Systems*, BS 5306: 1976– *Fire Extinguishing Installations and Equipment on Premises*, Part 5: 1982– *Halon Systems* and BS 6535: 1989– *Fire Extinguishing Media*, Part 2: 1989– *Halons*, Section 2.1: 1989 *Specification for Halon 1211 and Halon 1301* and Section 2.2: 1989 *Code of Practice of Safe Handling and Transfer Procedures.*

16.30.1 Mechanisms of fire extinguishment

Vaporizing liquids act against fire by essentially the same two mechanisms of interruption of the chain reactions and of blanketing. Treatments of the inhibition mechanisms and general theory of vaporizing liquids are given by Belles and O'Neil (1957), Spence and McHale (1965), W.E. Wilson, O'Donovan and Fristrom (1969), Dixon-Lewis and Simpson (1977), P.F. Thorne (1978b), Westbrook (1982c) and Mitani (1983).

16.30.2 Types of vaporizing liquid

The substances used as vaporizing liquids are halogenated hydrocarbons. They include the following classes: halon (H), hydrofluorocarbon (HFC), hydrochlorofluorocarbon (HCFC) and perfluorocarbon (PFC). The halons contain bromine and the perfluorocarbons contain fluorine as the only halogen.

Prominent halons are:

Halon 1211 Bromochlorodifluoromethane (BCF) CF_2ClBr
Halon 1301 Bromotrifluoromethane (BTM) CF_3Br

HCFCs include:

HCFC-22 Chlorodifluoromethane $CHClF_2$
HCFC-124 Chlorotetrafluoroethane C_2HF_4Cl

Vaporizing liquids are available which are much more effective extinguishants than carbon dioxide. Table 16.87 shows the relative effectiveness of various vaporizing liquids in extinguishing a hexane test fire (Hearfield, 1970). Whereas a concentration of 28% was required for carbon dioxide, the concentrations required with the vaporizing liquids were as shown in the table.

One of the most efficient extinguishing agents is Halon 1301. The relative fire extinguishing capability of other vaporizing liquids may be expressed in terms of the relative mass extinguishing efficiency (RMEE), defined as the ratio of the mass extinguishing concentration of the agent to that of Halon 1301 in a standard test. One such standard test is the ICI cup burner test.

Halon 1211, or bromochlorodifluoromethane (BCF), is now the principal vaporizing liquid. A comparison at 20°C of Halon 1211 with carbon dioxide shows that the specific gravities relative to air are 6.5 and 1.52 and the vapour pressures 2.61 and 57.2 bar, respectively.

Table 16.87 *Extinction of hexane test fire by vaporizing liquids (after Hearfield, 1970)*

		Hexane fire extinction (% v/v)
Bromochlorodifluoromethane (BCF)	CB_rClF_2	5.2
Dibromodifluoromethane	CBr_2F_2	3.6
Trifluoromethyl bromide	CF_3Br	4.2
Chlorobromomethane	CH_2ClBr	6.4
Methyl bromide	CH_3Br	7.7
Carbon tetrachloride	CCl_4	9.9

Thus BCF gives a better blanketing action and does not require such high strength containers.

Halon 1211 is a very effective extinguishing agent for flammable liquid and electrical fires. It is electrically non-conducting. Its cooling capacity, however, is low (latent heat 134 kJ/kg). It is capable, therefore, of dealing with a small solids fire but not with a large one.

Most Halon 1211 and Halon 1301 systems are of the total flooding type used to protect an enclosed space. The concept is that the halon is injected into the space and develops an approximately uniform concentration capable of extinguishing a fire anywhere in the enclosure. The alternative method of deployment of halon systems is local application in which the jet of halon is directed at the seat of the fire.

It is usually desirable to follow up the extinction of fire by Halon 1211 with water or foam cooling. This does not apply, however, to electrical fires or to situations where electrical equipment is near the seat of the fire.

16.30.3 Properties of vaporizing liquids

Vaporizing liquids may be ranked in respect of their effectiveness in extinguishing fires according to their performance in tests. There are numerous tabulations of relative effectiveness in particular tests.

Properties of a vaporizing liquid which bear on its effectiveness as a fire fighting agent include (1) chemical action, (2) vapour pressure and (3) density.

The ability to arrest combustion by interfering with the chain reactions is obviously a prime property.

The vapour pressure is significant in several respects. It determines the ability of the agent to discharge under its own pressure, the extent to which the flow in the pipework is two-phase and the behaviour of jet.

The density of the agent affects the mixing in the space into which is it discharged.

Compatibility with foams is another relevant property of vaporizing liquids.

In storage, early vaporizing liquids tended to give rise to corrosion problems. Halon 1301 and Halon 1211 have little corrosive action, provided that free water is not present.

16.30.4 Hazards associated with vaporizing liquids

There are certain toxic hazards associated with the use of vaporizing liquids. These include the toxic effects of (1) the agent, (2) the breakdown products of the agent and (3) the combustion products of the fire.

The first vaporizing liquid used was carbon tetrachloride, which is toxic. It was superseded by methyl bromide, which is highly toxic. Dibromofluoromethane is a convulsant. Chlorobromomethane is moderately toxic and produces narcosis. Bromochlorodifluoromethane (BCF) has a low acute toxicity. Bromotrifluoromethane (BTM) has an even lower acute toxicity, but also a very low boiling point (−58°C), so that contact can cause freezing of the skin and eyes by evaporation.

Vaporizing liquids give rise to decomposition products in fires. Halon 1211 yields the products hydrogen chloride, hydrogen bromide and hydrogen fluoride, which are extremely irritating to the eyes, nose and throat.

D.W. Moore (1986) gives the following approximate lethal concentrations of the natural vapour and of the decomposed vapour for a 15 minute exposure:

	Lethal concentration (ppm)	
	Natural vapour	*Decomposed vapour*
Methyl bromide	5 900	9 600
Bromochlorodifluoromethane	324 000	7 650
Bromotrifluoromethane	832 000	14 000

The toxicity of the combustion products of the fire is another significant factor in fire fighting using vaporizing liquids.

16.30.5 Delivery systems for vaporizing liquids

Vaporizing liquids are delivered to the fire mainly by fixed systems. They are also one of the agents used in portable extinguishers. Vaporizing liquids are less suitable for delivery from cylinders by hand held hose line or from mobile equipment. In addition, vaporizing liquids are used in fixed systems to suppress combustion inside plant.

16.30.6 Applications of vaporizing liquids

Vaporizing liquids are used to extinguish fires. They are utilized for this purpose in enclosed spaces, and in portable extinguishers. They are also used to suppress incipient combustion inside plant.

16.30.7 Fixed vaporizing liquid systems

Fixed vaporizing liquid systems may be (1) total flooding systems or (2) local application systems.

The hydraulics of some vaporizing liquid systems may involve two-phase flow. Although Halon 1211 can usually be treated as a single liquid phase in the pipework, Halon 1301, which exists as a single liquid phase in storage, begins to vaporize as it travels down the pipe. The flow characteristics of halon systems are discussed by Williamson (1976) and Wiersma (1978). Computer programs for halon hydraulics have been developed by suppliers.

Halon systems tend to be subject to corrosion. The problem is discussed by Peissard (1982).

16.30.8 Vapour retention tests

A feature of interest for a space protected by a halon system is the retention time of the halon. A method for the determination of this has been developed by the NFPA based on its Enclosure Integrity Test. In this integrity, or pressure, test, portable fan equipment is used to create a pressure difference between the protected volume and the surrounding space. Measurements are made from which the effective leakage area of the enclosure can be estimated. This is then used to calculate the halon retention time. Vapour retention tests are discussed by Genge (1989), Sreeves (1989) and Whiteley (1989).

16.30.9 Precautions

As stated earlier, guidance on the precautions to be taken to counter the toxic and asphyxiation hazards of

halon and of inert gas extinguishing systems is given in GS 16. There are a number of general precautions to be taken with any gaseous extinguishing system. If the system is an automatic one activated by rapid response fire detectors, two separate detection signals should be provided in order to reduce the frequency of false activations. The space protected should be provided with warning signs at all entrances. There should be an indication as to whether the system is set for manual or automatic activation.

If the system is a manually activated one, the release devices should be so located such that the person operating the device is not at risk from the fire or the discharge of the agent. For a total flooding system, activation of the system should be accompanied by an audible alarm distinct from the fire alarm. The entrances should have continuous warning signs which remain on until the space has been certified as fit to re-enter. There should be suitable escape routes. The space should be provided with adequate means of ventilation after a fire and/or discharge of the agent.

The installation should be covered by a safe system of work. The system should be subject to regular inspection by a competent person. GS 16 states that such an inspection should be done not less than twice a year and should result in an inspection report. It also details the precautions to be taken during maintenance. One measure required is the provision of a means of isolating the agent storage tank for maintenance or other circumstances where normal escape might be difficult.

GS 16 gives guidance on the selection of the agent and the system. The choice should have regard to the hazards to personnel. A local application system tends to involve less risk of personnel being trapped and may be preferable in some circumstances. If a total flooding system is used, the volume of the space protected should be kept to a minimum and the design should avoid excessive concentrations of the agent.

Account should be taken of the possibility that discharge of the agent may raise a dust cloud, with the attendant risk of a dust explosion.

With regard to the precautions which relate specifically to the agent, for a total flooding system using Halon 1211 the system should ensure that discharge does not occur whilst personnel are present. For a local application system for Halon 1211 the requirement is to design so that there is no foreseeable risk of a hazardous concentration being produced.

For Halon 1301 the precautions required are related to the concentration of the agent which may be attained. GS 16 states that, provided the concentration of this halon will not exceed 6%, and subject to certain other qualifications, an automatic total flooding system may be used to protect a normally occupied space. The space should be evacuated before the concentration of Halon 1301 exceeds 6%. It may be appropriate to incorporate a short time delay and pre-discharge alarm, but in order to ensure rapid response to the fire, the delay should not usually exceed 30 seconds.

16.30.10 Halon phase-out

The discovery by Molina and Rowland (1974) that chlorine can act as a catalyst for the conversion of ozone to molecular oxygen in the upper atmosphere initiated a growing concern for the state of the ozone layer. It was subsequently shown that halons have a particularly damaging effect.

This has led to the Montreal Protocol on Substances that Deplete the Ozone Layer, 1987, which lays down a programme for the phasing out of halons. Amendments to the treaty have been made at meetings in 1990 and in November 1992. Accounts of the Montreal Protocol and its implications for halon systems are given by Senecal (1992a,b), Hough (1993) and Simmonds (1993). The halons discussed are primarily Halon 1211 and Halon 1301. The original Montreal Protocol provides that the production of halons be reduced to 50% of the 1986 level by 1994 and to 0% by 1999.

With regard to the continued use of existing halon systems and to the recycling of halons for use in such systems, national policies vary. Germany has banned the use of halon fire fighting systems. According to Simmonds, in the absence of a suitable halon destruction technology, it is current policy not to dismantle the systems or return them to the suppliers but to let them remain on site capped off.

In the USA it is government policy to permit continued use of existing systems and the recycling of halons for use in such systems.

The UK also is evidently moving towards a policy of permitting continued use of existing systems, as evidenced by the HSE draft guidance on *Gaseous Fire Extinguishing Systems*.

Amendments to the Montreal Protocol also cover HCFCs, the production of which is to be frozen at 1989 levels and phased out by 2030, or possibly earlier.

16.30.11 Halon replacement and clean agents

The demise of the use of halons has led to a search for alternatives. These alternatives include both other vaporizing liquids and agents other than vaporizing liquids. Alternatives to halons have been reviewed by the Halons Technical Options Committee (G. Taylor, 1991) of the UN Environment Programme (UNEP). Other accounts of alternatives include those by Senecal (1992a,b), Hough (1993), McKay (1993) and Simmonds (1993). NFPA 2001: 1994 deals with clean agent alternatives to halons.

A review of vaporizing liquids used or proposed for use as fire extinguishing agents is given by Senecal (1992b), who covers HCFCs, HFCs and PFCs as well as CO_2, with a comparative tabulation of relevant properties and a detailed discussion of each agent.

Hough (1993) also reviews alternatives, but ranges more widely, from designing out of the need, through other vaporizing liquids, notably HCFCs, to foam, dry powder and fogging systems.

An account of work on the latter has been given by McKay (1993). Building on research on burner nozzle technology, a fine water spray system has been developed which uses water droplets in the diameter range 80–200 μm and is claimed to be a highly effective suppressant alternative to halons.

16.31 Fire Protection Using Inert Gas

The last of the principal fire fighting agents is inert gas. Here a distinction needs to be made between the use of inerting of equipment to prevent internal fire or explosion, as described in Chapter 17, and the use of inert gas to extinguish fire, which is considered here.

Accounts of the use of inert gas for fire extinguishment include those by Burgoyne, Katan and Richardson (1949b), McGuire (1964) and Bryant (1991). Fire protection using inert gas is treated in the NFPA *Handbook* by P.F. Johnson (1986) and, for carbon dioxide, by Williamson (1986).

Relevant codes and standards are NFPA 12: 1993 *Carbon Dioxide Extinguishing Systems* and BS 5306: 1976– *Fire Extinguishing Installations and Equipment on Premises*, Part 4: 1986 *Specification for Carbon Dioxide Systems* and BS 7273: *Code of Practice for the Operation of Fire Protection Measures*, Part 1: 1990 *Electrical Actuation of Gaseous Total Flooding Extinguishing Systems*.

16.31.1 Mechanisms of fire extinguishment

Extinguishment of fire by an inert gas is effected by reducing the concentrations both of the fuel and of oxygen. Design of an inert gas system is based on reducing the concentration of oxygen below that which will support combustion. A further, more recently favoured, mechanism is the reduction of the flame temperature below that necessary for combustion – the thermal ballast effect.

Inert gas also has a cooling effect. A large mass flow of gas over a liquid surface can be beneficial in preventing ignition when the discharge ceases and the liquid again comes in contact with air. These latter mechanisms indicate that it is desirable that the inert gas have a high heat capacity.

16.31.2 Types of inert gas

The principal individual inert gases used in fire protection applications are carbon dioxide and nitrogen. Use is also made of inert gas mixture formulations.

16.31.3 Properties of inert gas

Properties of an inert gas relevant to its use fire protection include (1) its density, (2) its vapour pressure, (3) the minimum concentration required for extinguishment and (4) its gas specific heat.

The density of the gas affects both its 'throw' and its subsequent flow.

The vapour pressure is relevant to the ability of the gas itself to provide the pressure necessary for discharge. An advantage of carbon dioxide, for example, is that its vapour pressure at room temperature is high enough to give satisfactory discharge.

The minimum concentration for extinguishment sets the lower limit of concentration of inert gas to be used. Information on this minimum concentration has been given by Coward and Jones (1952 BM Bull. 503), and has been widely reproduced. Values for carbon dioxide are tabulated by Williamson (1986).

As just indicated, a high gas specific heat is beneficial in that it enhances the thermal ballast and cooling effects of the inert gas. This is one of the advantages of carbon dioxide with its high heat capacity.

16.31.4 Hazards associated with inert gas

The two principal inert gases used are carbon dioxide and nitrogen. Carbon dioxide is mildly toxic, but the main hazard with both gases is that of asphyxiation. This hazard is present in all fire situations, but insofar as the extinguishment of fire requires high concentrations of inert gas the hazard is enhanced.

The density of the gas is relevant to the asphyxiation hazard; the density of nitrogen is close to that of air, whilst that of carbon dioxide is appreciably greater, so that it may accumulate in low lying spaces.

16.31.5 Delivery systems for inert gas

Inert gases are delivered to the fire by fixed systems, but not normally by mobile systems. The inert gas carbon dioxide is one of the agents used in portable extinguishers. In some cases hand held hose lines from cylinders are used to supplement a fixed delivery system.

16.31.6 Applications of inert gas

Inert gases are used to extinguish fires. They are utilized for this purpose in enclosed spaces, and in portable extinguishers.

16.31.7 Fixed inert gas systems

Inert gases are used in (1) total flooding systems, (2) local application systems and (3) hand held hose lines.

In a total flooding system the inert gas is injected into an enclosure in sufficient quantity to ensure the minimum concentration for extinguishment.

In a local application system a jet of inert gas is directed at the surface protected, which is typically a tank surface but may also include the adjacent floor area. There is a minimum discharge time for effective extinguishment, that recommended for carbon dioxide being 30 seconds.

For carbon dioxide, hand held hose lines from cylinders are also used.

16.31.8 Precautions

The precautions given in GS 16 for halon and inert gas extinguishing systems have been outlined in the previous section. Those for an inert gas are broadly similar to those for Halon 1211. The essential requirement is to ensure that operation of the system does not expose personnel to hazardous concentrations. For a total flooding system this means that the arrangement should prevent the system from operating when personnel are present, whilst for a local application system the requirement is to design so that there is no foreseeable risk of a hazardous concentration being produced.

16.32 Fire Protection Using Special Methods

In addition to the methods just described, there are also several special methods of fighting fires. They include the use of (1) solids and powders, (2) wet water or wet water foam and (3) combined agent systems. Fire protection using such special methods is treated in the NFPA *Handbook* by P.F. Johnson (1986).

16.32.1 Solids and powders

In addition to dry chemicals, use is also made of various kinds of dry powder, sand and other solid materials. One group of solid agents comprises those used for metal fires, e.g. talc, soda ash and graphite.

Another solid agent is glass granules used for the control of LNG bund fires (Lev, 1981). The granules are stored within the bund and, when an LNG spill occurs, they float to the top. The mechanism of action is reduction of the radiation from the flame to the surface and thus of the evaporation of the fuel.

A third solid agent is carbon microspheres used for extinguishment of metal fires (McCormick and Schmitt, 1974).

Treatments of the extinguishment mechanisms of dry powders, including inert particulates, are given by Dolan (1957), McCamy, Shoub and Lee (1957), Morikawa (1976) and G. Russell (1977).

The provision of sand buckets for dealing with small fires has long been common practice on process plant. Sand is also used for diking in, and thus containing, liquid spillages.

16.32.2 Wet water and wet water foam

A second special method is the use of wetting agents to modify the properties of water, thus producing 'wet water'. A relevant code is NFPA 18: 1990 *Wetting Agents*.

In this context a wetting agent is one which, when added to water, effects a substantial change in its surface tension, thus increasing its ability to penetrate and spread. The wetting agent may also impart emulsifying and foaming characteristics.

The use of a wetting agent makes the water more 'effective' so that less is needed. This is of particular value in fire fighting where water is in short supply. A typical application is to forest fires.

If the wetting agent has suitable foaming qualities, a wet water foam is produced.

Fixed water sprinkler and water spray systems, as described in NFPA 13 and NPFA 15, may be designed to operate on wet water.

16.32.3 Combined agent systems

A third special method is the use of a combination of agents. An early application of the combined agents technique was the use during World War II of a combination of carbon dioxide and foam to attack a spill of aviation fuel from an aircraft and so rescue the aircrew.

Some agent combinations used are (1) water and foam, (2) carbon dioxide and foam and (3) certain dry chemicals and foam. Thus foam is prominent as one of the agents in such combinations.

In some cases the agents are applied simultaneously, in others they are used in rapid succession. A typical case of the application of a dry chemical and foam combination might be to extinguish fire on a flammable liquid by a large but short discharge of dry chemical and then to blanket the liquid with foam to prevent reignition.

16.33 Fire Protection using Portable Extinguishers

So far only passing reference has been made to portable fire extinguishers. These are, however, another important resource for fire protection. Accounts of portable fire extinguishers are given by Guccione (1961), Guise and Zeratsky (1965, 1982) and P. Nash (1969, 1991). Fire protection using portable fire extinguishers is treated in the NFPA *Handbook* by M.E. Petersen (1986a,b).

Relevant codes and standards are NFPA 10: 1990 *Portable Fire Extinguishers* and BS 5423: 1987 *Specification for Portable Fire Extinguishers* with its associated standard BS 6643: 1985– *Recharging Fire Extinguishers*. There are also a number of Underwriters Laboratories (UL) standards.

It is a fundamental principle of fire fighting that a fire should be hit hard and quickly, preferably before it has a chance to take hold. Usually the time which elapses before the fire brigade arrives is measured in minutes, even tens of minutes, and by then the fire may be well developed. For some hazardous items prompt response can best be achieved by an automatic fire protection system. For others, portable fire extinguishers provide the necessary means.

Conditions for success in the use of portable fire extinguishers are that the fire be small, that extinguishers be accessible, that they be of the right type, that they operate when activated and that personnel capable of using them are present.

These conditions have a number of implications. The potential sources of fire need to be identified and extinguishers with appropriate agents located at suitable points. The selection and maintenance of the extinguishers should take account of any potential unrevealed failure. Personnel should be trained in their use.

Fires of combustible materials (NFPA Class A), flammable liquids (Class B), electrical equipment (Class C) and metals (Class D) can all be dealt with by the use of suitably chosen portable fire extinguishers.

Principal agents used in portable fire extinguishers are (1) water, (2) foam, (3) carbon dioxide, (4) dry chemicals, (5) vaporizing liquids and (6) dry powders. Broadly, water is used on Class A fires and foam (AFFF) on Class B fires. Carbon dioxide and suitable dry chemicals and vaporizing liquids (Halon 1211) are used on fires of Classes A–C and dry powder is used on Class D fires. Some dry chemicals are suitable for fire Classes B and C and others for Classes A–C. A detailed tabulation of agents and their applications is given by M.E. Petersen (1986b).

There are several different principles of operation of a portable fire extinguisher. For water and foam extinguishers the three traditional types have been: (1) stored pressure, (2) pump tank and (3) inverting. In a stored pressure type the agent is expelled by an expellant gas held in the same chamber. In a pump tank type expulsion of the agent is effected by pressure generated by operation of the hand pump. The inverting type has been obsolete for some years; manufacture in the USA ceased in 1969. The agents used only in this type, soda acid and foam, have also become obsolete.

Other portable extinguishers utilize (1) stored pressure, (2) cartridge or (3) self-expulsion methods. As just explained, in the stored pressure type, the agent and expellant gas are held in the same chamber, whilst in the cartridge type the expellant is held in a separate cartridge. Dry chemical extinguishers use both stored pressure and cartridge methods. Halon 1211 extinguishers tend to use stored pressure. In carbon dioxide extinguishers the agent is self-expelling.

16.34 Fire Protection Applications

Fire fighting applications in process plant may be classified according to the material on fire or according to the plant and storage protected. The applications considered here are, by material, (1) combustible solids fires, (2) flammable liquid fires, (3) electrical fires and (4) metal fires and, by plant or storage (1) storage tanks and (2) warehouses.

16.34.1 Combustible solids fires

A type of fire common in all occupancies is a combustible solids fire (NFPA Class A). In the process industries combustible solids occur in bulk and powder forms both in process and in storage. Process operations which typically involve combustible solids include dust handling plant, conveyors and packaging plant. Storage sites such as silos and warehouses may contain large quantities of combustible solids.

There are a number of NFPA codes covering particular solid materials. They include NFPA 43A (oxidizers), NFPA 43B (organic peroxides), NFPA 490 (ammonium nitrate), NFPA 654 (powders and dusts) and NFPA 655 (sulphur). Other NFPA codes for metals are given in Section 16.34.4.

Fixed fire protection systems are provided in selected cases. The design options depend on the situation. For example, a total flooding design is practical only if the solids are being handled in an enclosure and it will not endanger personnel.

Where solids are handled indoors, regard should be had to the potential difficulties of fighting the fire once it has taken hold and is producing large volumes of smoke. It may be only minutes before entry into the building becomes impossible. This implies that any fixed fire protection system should respond rapidly and strongly.

The fire protection of warehouses is considered further in Section 16.34.7.

16.34.2 Flammable liquid fires

Another type of fire common in the process industries particularly is a flammable liquids fire (NFPA Class B). Process industry activities involve the processing and storage of a wide variety of flammable liquids. Storages may contain large quantities of flammable liquids.

Fixed fire protection systems are provided for process operations and areas vulnerable to releases and spills, for loading and unloading facilities and, above all, for storage tanks and vessels. Storage tanks are commonly provided with a bund. It is therefore necessary to protect not only against a fire in the tank itself but also against one in the bund.

The fire protection of storage tanks in general is considered further in Section 16.34.6. Further accounts of the protection of particular types of storage tank such as LPG, LNG and ammonia tanks are given in Chapter 22.

16.34.3 Electrical fires

There are also certain special types of fire that require treatment, one of which is the electrical fire (NFPA Class C). If electrical equipment is involved in a fire on a process plant, this is generally due to an explosion at the equipment itself or to a spread of a fire from the rest of the plant. If there is a fire at a piece of live electrical equipment, it is usually appropriate to de-energize the equipment, unless there are good reasons for not doing so.

In respect of fire, electrical equipment may be divided into (1) equipment which has exposed contacts and (2) equipment such as transformers and circuit breakers.

Among the agents used on electrical fires are water, dry chemicals, vaporizing liquids and inert gases, but not all agents are suitable for every type of electrical fire.

Water as a continuous jet conducts electricity and should not be used in this form on electrical fires. In the form of spray, however, this hazard is much less and is generally negligible (O'Dogherty, 1965).

Some electrical equipment is protected using a fixed water spray system. Water sprays are used, for example, to protect against fires in oil cooled electrical equipment such as transformers. Such a fire is generally the result of an electrical breakdown which causes an explosion. Such mixed fires of hot oil and hot metal are difficult to handle. Typically the oil is being pumped over metal surfaces which become hot and sustain the fire. It is important, therefore, to ensure that such situations are detected and dealt with as early as possible. The protection of such electrical equipment with water sprays is a specialist matter. It is discussed by P. Nash (1974a).

Fixed systems for the protection of electrical equipment tend to use dry chemicals or carbon dioxide. As already stated, the former is not suitable for equipment with exposed contacts which are liable to suffer adhesion and corrosion. Fires of electrical equipment are mainly fought using portable carbon dioxide or dry chemical extinguishers.

16.34.4 Metal fires

Another type of fire which requires special treatment is metal fires (NFPA Class D). Accounts of metal fires and methods of dealing with them are given by Reuillon *et al.* (1977), Sharma, Lal and Singh (1987), Varshney, Kumar and Sharma (1990), Cardillo and Nebuloni (1992) and Sharma, Varshney and Kumar (1993). Metal fires are treated in the NFPA *Handbook* by Prokopovitsh (1986) and by P.F. Johnson (1986).

The NFPA codes on the storage of certain metals are of some relevance. These are NFPA 48 (magnesium), NFPA 481 (titanium) and NFPA 482 (zirconium).

Metal fires involve a number of hazards. Characteristic hazards are (1) extremely high temperatures, (2) steam explosion and (3) hydrogen explosion, as well as the usual hazards of (4) toxic combustion products and (5) oxygen depletion.

Extinguishment of a metal fire is not always achievable and it may be necessary to settle for control of the fire. The agent used should be matched to the metal; an agent suitable for dealing with a fire of one metal may be quite unsuitable for that of another. Water should not be used on a sodium fire, and a vaporizing liquid should not be used on a magnesium fire. That said, there are some powder agents which are suitable for fires of several metals, as described below.

Combustible metal extinguishing agents are classified according to whether they are (1) approved or (2) proprietary. Approved agents are those proprietary agents which are tested and approved by organizations such as the UL. There are also proprietary agents and non-proprietary agents.

Prominent proprietary agents are Pyrex G1 powder, which is a coke powder with an organic phosphate additive. Metalguard powder has a similar formulation. Another agent is Met-L-X powder, which has a sodium chloride base, again with additives. Prokopovitsh gives a tabulation of the comparative capabilities of G1 and Met-L-X powders in dealing with fires of a number of metals, including aluminium, magnesium, sodium, potassium, titanium, zirconium and lithium. He also discusses the use of other proprietary agents and of non-proprietary agents such as talc powder, soda ash, salt and sand.

16.34.5 Storage tanks

Turning to the fire protection of particular plant and storage, protection of storage tanks is a prominent theme. Accounts of fire protection of storage tanks and bunds are given by A.H. Warren (1966), Hearfield (1970), J.R. Hughes (1970), Vervalin (1973f), P. Nash and Young (1975 BRE CP42/75), Peyton (1984) and M. Wilson (1993). Fire protection of storage tanks is treated in the NFPA *Handbook* for flammable liquids by M.F. Henry (1986) and for chemicals by Bradford (1986b).

Relevant codes and standards for storage tanks, including low temperature storages, are NFPA 30: 1990, API Std 620: 1990 and API Std 650: 1993, and BS 799: 1972–, BS 2654: 1989, BS 4741: 1971 and BS 5387: 1976. There are also codes for the storage of particular chemicals such as NFPA 43A: 1990, which covers liquid oxidizers.

Fire protection of a storage tank needs to address several different scenarios: (1) a fire near to the tank, (2) a fire in the top of the tank and (3) a fire in the bund. There are therefore requirements for exposure protection by cooling of the tank and for fire extinguishment and control in the tank itself, in the bund and of a liquid spill outside the bund.

Among the facilities which may be provided for the fire protection of a storage tank are (1) fire resistant thermal insulation or fire insulation, (2) a fixed water system for cooling, (3) a fixed foam system for the tank top, (4) a fixed foam system for the bund, (5) fixed water/foam monitors and (6) mobile water/foam monitors. There may also be a role for fixed water spray systems for the extinguishment and control of liquid spills.

Foam systems for storage tanks have been discussed in Section 16.28. A further account of fire protection of storage tanks is given in Chapter 22. Fire fighting on storage tanks is discussed in the next section.

16.34.6 Storage vessels

The fire protection of storage vessels, particularly those containing liquefied flammable gas, is equally important. Accounts of the fire protection of storage vessels are given by Pettit (1945), Bray (1964, 1966), Chaillot (1966), the FPA (1966), ICI/RoSPA (1970 IS/74), Eijnhoven, Nieuwenhuizen and Wally (1974), I. Williams (1984) and B.M. Lee (1989). Fire protection of storage vessels for LFG is treated in the NFPA *Handbook* by Walls (1986).

Relevant codes and standards for storage vessels for LFG are NFPA 54: 1992, NFPA 58: 1992, NFPA 50: 1990, NFPA 59A: 1990, the ASME *Boiler and Pressure Vessel Code*, Section VIII and BS 5500: 1991. NFPA 50: 1990 covers liquid oxygen and NFPA 50A: 1989 and NFPA 50B: 1989 cover gaseous and liquid hydrogen, respectively.

Among the facilities which may be provided for the fire protection of a storage vessel are (1) drainage, including sloped ground, (2) fire resistant thermal insulation or fire insulation, (3) a fixed water system for cooling and (4) depressuring facilities.

A further account of the fire protection of storage vessels is given in Chapter 22.

16.34.7 Warehouses

Warehouses are another type of storage which contain large quantities of combustible material. The account here is limited to fire protection systems; a fuller account of warehouses, including prevention of fire, is given in Chapter 22.

Accounts of fire protection of warehouses include those by P. Nash (1972a, 1977), P. Nash, Bridge and Young (1974 BRE CP68/74), Bridge (1977), Young and Nash (1977), Parnell (1979), Field (1985), Murrell (1988) and Murrell and Field (1990).

Much of the work described by these authors was conducted at the Fire Research Station, with one programme in the mid-1970s (e.g. FRS, 1972 Fire Res. Note 914, 916, 944; P. Nash, 1977) and another in the mid-1980s (e.g. Field, 1985; Murrell, 1988). A relevant code is NFPA 231C: 1991 *Rack Storage of Materials*.

The fire problem is particularly acute in automated high bay, or high rack, warehouses. The FRS work has shown that in such situations fire develops rapidly, with flames propagating upwards, mainly in the flues between adjacent pallets. The fire typically reaches the top of the rack within 2 minutes. It becomes virtually impossible to fight the fire by conventional means.

The earlier FRS programme also showed that conventional sprinklers with glass bulbs set to operate at 68°C do not respond quickly enough to counter the fire before it gains hold. An alternative system was developed in which the bays are zoned with sets of sprinklers dedicated to a zone and actuated by a fire detection wire 'laced' through the racking. This system was criticized as being too complex and liable to false alarms and was not taken up by industry.

The later programme, described by Field (1985), concentrated on the response of the sprinkler head. A solder-link sprinkler was identified which proved satisfactory. For a single localized ignition source the sprinkler system operated to extinguish the fire with a maximum water volume of 350 UKgal.

16.35 Fire Fighting in Process Plant

The foregoing account has described some of the passive measures used to prevent fire and to protect against it and some of the agents and equipment available for active measures of actual fire fighting. It is now necessary to discuss some of the general principles underlying fire fighting in process plants, bearing in mind the wide variety of types of fire which may be encountered.

General accounts of fire fighting are given in *Manual of Firemanship* (Home Office, 1974–), *Fire Fighting in Factories* (HSE, 1970 HSW Bklt 10) and *Fire Attack, Fire Service Communications for Fire Attack* and *The Extinguishment of Fire* (NFPA, 1966/4, 1972/8, 1974/11). Fire fighting in the process industries and with chemicals is discussed in *Fire Protection Manual for Hydrocarbon Processing Plants* (Vervalin, 1964a, 1973a) and the *Fire Training Manual* (PITB, 1975/6) and by several other authors, particularly Risinger (1964b,c,f,g).

In most fire fighting operations on process plant it is necessary not only to fight the fire but also to protect the vessels exposed to it. This second activity is just as important as the first.

A fundamental principle of fire fighting is to attack the fire at as early a stage as possible and to hit it hard. Once a fire is well established and has heated up large quantities of metal and liquids, it becomes much more

difficult to contain it and prevent it growing. There are a number of case histories, described in Appendix 1, which illustrate the problems of fire fighting in process plants.

16.35.1 Liquid fires

There are two important distinctions to be made in considering fire fighting of burning liquids. One is that between (1) contained fires and (2) uncontained fires. A liquid fire is contained if the liquid is held in a well defined container such as a storage tank, bund or deep depression. In other situations, such as spillages or pools, the liquid fire is uncontained. In some cases it may even be flowing.

The other distinction is between fire of (1) high flashpoint liquids and (2) low flashpoint liquids. A liquid with a high flashpoint can generally be extinguished by cooling with water, whereas one with a low flashpoint usually needs to be blanketed by foam or dry chemicals.

Contained fires of either high or low flashpoint liquids can normally be extinguished by foam. Fires of contained high flashpoint liquids can alternatively be extinguished by cooling with water.

With a highflash point product, such as refined oil, the rise in liquid temperature is generally confined to a layer of about 2 in. (5 cm) below the liquid surface, even when the liquid has been burning for a long time. In consequence, when water or foam is added, the heat in the liquid is generally not sufficient to cause an oil–water slopover, unless the surface is very close to the top of the container.

The fact that the bulk oil remains relatively cold means that it is also possible to cool the surface layer by agitating the oil. This may be done, for example, by directing a fire water jet down into the liquid.

It sometimes occurs that a high flashpoint liquid is contaminated by error with some low flashpoint material. Usually the amount of contaminant does not exceed 5%. In such cases the more volatile material tends to burn off in the early stages of the fire, leaving an essentially high flashpoint liquid again.

With uncontained fires the first step is generally not to extinguish the fire but to cut off the flow of liquid from the containment. If such a fire is merely extinguished without cutting off the flow of fuel, there is a serious risk that it will re-ignite and cause a much larger fire or possibly an explosion. It is difficult to overemphasize the importance of this point. To quote Risinger (1964g): 'It is more important to know when not to put a fire out than to know the details of actual extinguishment.' With low flashpoint liquids the risks include that of a vapour cloud explosion.

Often the flow of liquid may be stopped by shutting off an emergency isolation valve. It is good practice that such valves should have remote operation for just this situation. Where it is necessary to approach the fire in order to close a valve, a water fog may be used to provide a shield from the heat.

Another device which may be adopted where a flammable liquid which has a density below that of water is flowing from a pipe connected to the bottom of a tank, is to inject water into the tank and so replace the liquid flowing through the pipe with water.

An uncontained fire of a high flashpoint liquid can generally be extinguished by the use of water. For a fire on a low flashpoint liquid, foam or dry chemicals should normally be used.

Often where dry chemicals are used, it is necessary to use water also. Although the former are effective in putting out the fire, there is generally a high risk of re-ignition from the metal which has been heated by the fire. Typically, it is necessary to apply water to cool this metal, then use dry chemicals to extinguish the fire, and then apply water again to cool the liquid.

With dry chemicals the quantity which can be used and therefore the time of application are both strictly limited, the latter being generally of the order of some tens of seconds. It is essential, therefore, to put the fire out in the initial attack.

In some cases there are simultaneous contained and uncontained fires. A typical example is burning petroleum liquid flowing over the side of a storage tank. In such a case the procedure is to put out the uncontained fire first. If this is done, the uncontained part does not readily re-ignite because the more volatile components have already been burned off in the tank, whereas if the converse approach is taken, the spillage does tend to be re-ignited by flame travel over the liquid surface.

It is not always either practical or desirable to extinguish a liquid fire. It is generally impractical, for example, to extinguish a very large fire of LPG in an open container or spillage. Moreover, even if it were, extinction of the fire would create the risk of a vapour cloud explosion.

The procedure in such cases, therefore, is to cut off the flow of liquid to the fire, to cool the container and other exposed surfaces and to seek not to put out the fire itself but to control it. It is particularly important to cool the surface of tanks above the liquid level. If the fire is causing any blowtorch effect, the area affected by this should also be cooled.

The use of large quantities of water, or to a lesser extent foam, involves the hazard of spreading the fire by displacing and/or floating the burning liquid. This hazard should be borne in mind in fire fighting operations.

Further information is given by Risinger (1964g).

16.35.2 LFG fires

Fires of liquefied flammable gas (LFG) are often fought using dry chemicals or foam, or both in combination. Although the extinction of fire is generally desirable, it may not always be appropriate or possible. It is nevertheless a worthwhile objective to control the fire and so reduce the heat radiation from it.

Large-scale tests on the effectiveness of foam and of dry powder on fires have been carried out as part of the experiments by MITI (1976), described earlier. In one test liquid ethylene was poured into a 3 m diameter bund with a wire netting cover and ignited. An attempt was then made to extinguish the flame using high expansion foam with an expansion ratio of 500 from fixed foam generators with a combined output of 200 m^3/min. The first foam generator was started 2 minutes after ignition and the second 1 minute later. The rate of application of foam was 7.07 m^3/m^2 min. The foam brought the fire about 50% under control within about $3\frac{1}{2}$ minutes after ignition, and 80% under control just over 6 minutes after ignition. Thereafter the effectiveness of control remained unaltered. It was concluded that liquid ethylene fires can be kept under control using high expansion foam.

In another test the fire extinguishing agent used was dry powder of ammonium phosphate discharged from two vehicles near the bund. An initial discharge of dry powder for 7 seconds was observed to extinguish the fire, but a second discharge of 4 seconds was applied to make sure. The rate of discharge was 45 kg/s to an area of 20 m^2 and, assuming that 50–80% of the powder covered this area, the rate of application was 1.3–1.8 kg/m^2 s. This compares with a slightly higher rate of 2.4 kg/m^2 s reported from other Japanese work.

16.35.3 LNG fires

As already described, the quantities of LNG held in storage are very large. A fire on a large LNG spillage radiates intense heat and can do extensive damage. The behaviour of LNG fires was discussed in Sections 16.11 and 16.17.

As stated above, fire fighting will often be conducted with the aim of controlling rather than extinguishing the fire. The control of LNG fires has been the subject of investigations over a period of time and in a number of countries. Early work by Burgoyne and Richardson (1948) showed that foam forms a frozen blanket on burning liquid methane, leaving only small tears which can be readily extinguished with dry chemicals.

Small LNG fires can in fact be extinguished by most fire fighting agents. Thus water, foam, dry chemicals, vaporizing liquids and carbon dioxide are all effective on fires sufficiently small to allow the whole area of the fire to be extinguished simultaneously.

With larger LNG fires the problem is more difficult. The feasibility of extinguishing large LNG fires has been a matter of doubt. Walls (1973), for example, states: 'Foams and water will not extinguish LNG fires.'

Dry chemicals can extinguish an LNG fire, but only if extinction is complete in the short application period, which is difficult to achieve. He continues: 'An LNG fire extinguishing system should be considered essentially as a fringe benefit which will be nice if it works but which a plant had better be able to do without.'

The limitation of the effects of LNG fires is described by Wesson *et al.* (1973a) as follows:

> Water has long been considered the prime – if not the only – agent suitable for controlling LNG fires. Water curtains and direct contact water sprays protect exposed structures until fire intensity is tolerable. However, for major LNG spills or tank fires the rate of water application required is unrealistic (30 000–50 000 gpm) if several proximate exposures require simultaneous protection from the high radiant heat fluxes, which can reach 10 000 BTU/h ft^2.

The control of LNG fires by agents such as foam or dry chemicals has thus continued to appear attractive.

Work at Lake Charles, Louisiana, in 1961 on the extinction of LNG fires has been reported by Burgess and Zabetakis (1962 BM RI 6099). Tests were done using dry chemicals. The surface area of the burning liquid pools was 400 ft^2. Extinction was achieved using sodium and potassium bicarbonates at application rates of 0.14 lb/ft^2 s. In one test extinction was achieved in 3 seconds at this rate of application.

More recently an extensive series of tests on the extinction of large LNG fires conducted by the University Engineers has been sponsored by the American Gas Association (AGA) and has been reported by Wesson and co-workers. The control of LNG fires using foam is described by Wesson, Welker and Brown (1972) and by Wesson *et al.* (1973a). Twelve tests were conducted, of which eleven were concerned with fire control and one with vaporization behaviour. The surface areas of the burning pools were in the range 400–1200 ft^2. The fire conditions were steady state with an evaporation rate of approximately 0.5 in./min from the spillage surface. It was found that high expansion foam was effective in bringing the fire under control and thus reducing heat radiation, although in the majority of cases the fire was not actually extinguished, and that a foam with an expansion ratio of 500 : 1 was the most suitable. The foam quickly froze in open cellular form at the foam–LNG interface, and was light enough to float on the LNG, but had sufficient structural strength to support several feet of additional foam without collapsing. A fire control time was defined as the time for the heat flux sensors to reach a new, reduced reading after initial application of the foam and while the foam was still being applied. Using a high quality foam with a 500 : 1 expansion ratio, a fire control time of 120 seconds was achieved with a foam application rate of 8 cfm/ft^2. Reductions in heat radiation of up to 97% were measured at a distance of about one fire diameter from the fire edge.

Wesson *et al.* (1973b) also report work on the extinction of LNG fires using dry chemicals. The fire sizes were in the range 200–1200 ft^2. The dry chemical application rates and extinction times obtained for a 1200 ft^2 fire are given in Table 16.88. The work described applies to steady-state LNG fires with an evaporation rate of not more than 0.5 in./min. Immediately after a spillage the vaporization of LNG is very rapid. Even 1 minute

Table 16.88 *Application rates for extinction of LNG fires by dry powders (after Wesson et al., 1973b)*

	Threshold rate		*Optimum rate*	
	Application rate (lb/ft^2 s)	*Extinction time* (s)	*Application rate* (lb/ft^2 s)	*Extinction time* (s)
Sodium bicarbonate (SB)	0.012	18	0.019 2	9.0
Potassium bicarbonate (PB)	0.007	30	0.012 5	8.2
Urea–potassium bicarbonate (U-PBP)	0.002 75	25	0.004 17	10.9

after the initial spillage and ignition, the evaporation rate could be 1 in./min on average dry soil, which is twice the long-term burning rate due only to heat transfer by flame radiation to the liquid surface.

The effectiveness of the fire fighting agents depends on the fire conditions, including the weather, the ground and the process plant. The foregoing account should be regarded, therefore, only as a guide. Further details are given in the original papers.

16.35.4 Storage tank fires

The occurrence of storage tank fires was discussed in Section 16.11 and the pool fire characteristics of such fire in Section 16.17. A fire in a storage tank which has lost its roof may be dealt with in two ways. One is to try to extinguish it; the other is to let it burn itself out. Such a fire is normally extinguished by the use of water or foam. The blanketing action of the latter is particularly effective against fires in open storage tanks.

There is a risk, however, that the addition of water or foam may cause a slopover of oil-water mixture. This can occur if there is a deep layer of hot oil at the burning liquid surface. Such a layer tends to develop in a crude oil but not in a refined one. The depth of the layer is greater after the fire has been burning some time. The hazard of slopover may be detected by such methods as the addition of small amounts of water to one edge of the tank or the use of a strip of heat sensitive paint down the side of the tank. Methods of reducing the hazard include mixing the hot oil in the tank with cold oil, by pumping the liquid out and in again, or by using only small quantities of water or foam until frothing subsides. Alternatively, the fire may simply be allowed to burn itself out. Often it is possible to pump out most of the liquid in the tank to another receiver so that the scale and duration of the fire are much reduced.

As described in Section 16.17, in a storage tank fire a heat wave moves down through the liquid. The fire is sustained by a zone of liquid at the top which is at a higher temperature than the rest of the contents. This fact can be exploited to control a tank fire by agitating the liquid with air. The method is described by P.F. Johnson (1986).

Other fires at storage tanks include a fire or a liquid spillage at the base of the tank. In this case it is generally appropriate to attempt to extinguish the liquid fire or to run the burning liquid off while cooling the tank to prevent its overheating.

In general, the fighting of storage tank fires involves not only extinction of the fire itself but also protection of other exposed tanks. Suitable water application rates are given in Section 16.27. Storage tank fires are discussed by Risinger (1964b,f).

16.35.5 Fog nozzles

There is a wide variety of nozzles which can be fitted to fire hoses. Accounts of such nozzles are given by Purington (1986) and Rosenhahn (1986).

In certain situations the requirement is not so much to project water onto the fire as to permit the fire fighters to advance towards the fire. This might be the case, for example, where an attempt is to be made to shut a valve. In such cases use may be made of a fog nozzle, which is more fit for this purpose than a regular hose nozzle.

16.35.6 Water curtains

A technique which finds application in certain situations involving a leak or fire of a flammable material is the use of a water curtain. One application of a water curtain is to disperse a leak of flammable vapour, before it can ignite. This has been described by Beresford (1981) and is considered in Chapter 15. Although not strictly a fire fighting measure, the deployment of a such water curtain is likely to be the responsibility of the works fire service and to be made in a fire situation.

Another use of water curtains is to attenuate the thermal radiation from a fire. Accounts are given by Stephenson and Coward (1987), Maini and Stephenson (1989) and Coppalle, Nedelka and Bauer (1993). The first two sets of authors describe a project to explore the use of water curtains to protect the crew of a tanker as they make their way to lifeboats during a shipboard fire. The design basis fires and heat fluxes are described by Stephenson and Coward and the modelling of and full scale experimental work on the water curtain is described by Maini and Stephenson.

The issues to be determined were the stability of the curtain and its capability to attenuate thermal radiation. The aim was to design a curtain some 5 m high which would remain stable in a 6 m/s wind. The modelling showed that heat attenuation is effected by a curtain of small droplets, which thus has a large total surface area, falling at low velocity. Work on curtain stability showed that to obtain a stable curtain it was better to use narrow angle nozzles rather than wide angle nozzles. With the former the droplets leave with a high initial velocity and then decelerate so that the velocity becomes much lower. There was relatively little difficulty in obtaining stability in the initial zone of 2–3 m, but below this the curtain can become unstable. It was found that in order to achieve a stable curtain it was necessary to obtain a sufficient momentum flow, where

$$\text{Momentum flow} = \text{Mass flow} \times \text{Exit velocity}$$

and that for the nozzles used a minimum value of the momentum flow was some 60 Ns/s. Given a momentum flow in excess of this value, narrow angle nozzles provided a stable curtain.

Work on attenuation of thermal radiation was performed using fires with surface emissive powers of the order of 50 kW/m^2. It showed that in order to obtain adequate attenuation in the upper zone it was necessary to deploy, in addition, wide angle nozzles. One arrangement which gave good performance was narrow angle nozzles spaced at 1 m intervals with two wide angle nozzles in each interval. With this arrangement attenuation was effected in the upper zone by the small slow droplets from the wide angle nozzles and in the lower zone by the small, slowed droplets from the narrow angle nozzles. The fractional attenuations obtained ranged from 30% to 70%, being an approximately linear function of the optical thickness. Models were developed for the behaviour of the water curtain with respect to both stability and attenuation; the results for the latter show close agreement with the experimental values.

Commenting on this work, the authors state that the essential requirement for such a water curtain is the combination of high momentum flow with small droplet

size. The design which they favour is one with narrow and wide angle nozzles. They refer to the need for a water supply at a pressure of at least 5 barg. They indicate that the curtain should be stable in winds up to 6 m/s but not in very high winds.

16.35.7 Hazards to fire fighters

Fire fighting is always a hazardous task, but this is particularly so on a process plant. Some of the hazards encountered are:

(1) heat and flames;
(2) falling structures and brands;
(3) flashback;
(4) explosion;
(5) toxic fumes;
(6) asphyxiating fumes;
(7) refrigerated liquids;
(8) chemical hazards;
(9) hazards due to fire fighting activities –
  (a) spread of burning liquids,
  (b) slopover due to foam,
  (c) fumes from vaporizing liquids,
  (d) discharge of dry chemicals.

Many process plant fires involve liquids. These are difficult to extinguish and tend to re-ignite, particularly if there are areas of hot metal. There is a danger, therefore, that flashback of the fire may occur.

Fires often cause explosions in vessels, particularly those containing liquids. It is standard practice to cool vessels with water to lessen the chance of their rupturing or exploding, but nevertheless explosions do occur. Process plants also contain many other objects which may explode.

Large quantities of toxic fumes are frequently involved in fires. They may come not only from process materials but also from lagging and from fire fighting agents. In particular, hydrogen chloride and other acid gases are often produced.

Some materials produce more insidious fumes. For example, the fumes of toluene diisocyanate not only cause euphoria and lead firemen to undertake rash actions but also attack the nervous system and can lead to permanent disability. Outright asphyxiation due to lack of oxygen is another hazard in such fires.

Some liquid spillages involve refrigerated liquefied gases. Contact with these can cause freezing of and injury to parts of the body.

Fire causes loss of containment of other chemicals, such as corrosive substances, which constitute further hazards to personnel.

Some of the hazards arise from the fire fighting activities. The use of water may cause burning hydrocarbon liquids to spread, particularly into drains. The addition of foam to a tank where the fire has formed a hot zone can cause slopover. The fumes from vaporizing liquids tend to be highly toxic. The high velocity discharge of dry chemicals can cause injury.

Although local authority firemen should be generally familiar with the hazards of process plants in their area through training and exercises, it is important for them to be fully informed of the particular hazards presented by a fire which they are called on to fight.

16.35.8 Planning and training

It is essential to plan for emergencies and fires and to train personnel in emergency procedures and fire fighting. A detailed account of emergency planning is given in Chapter 24. This includes devising scenarios of accidents and conducting full-scale emergency and fire fighting exercises.

The *Fire Training Manual* of the Petroleum Industry Training Board (PITB) (1975/6) gives guidance on training for fire fighting related specifically to process plant fires.

16.36 Fire and Fire Protection in Buildings

The most serious fires, with respect both to loss of life and to damage, are those which occur in buildings. Although fire in buildings does not have the same relative significance for process plant, it is still important, because there are many plants which need to be housed in buildings and there are on virtually all sites a range of other buildings from laboratories, workshops and offices, to stores and warehouses.

Accounts of fire and fire protection in buildings are given in *Fire Safety in Buildings. Principles and Practice* (Langdon-Thomas, 1972), *Handbook of Industrial Loss Prevention* (FMEC, 1967), *Fire Protection Handbook* (NFPA, 1991/28) and *Background Notes on Fire and its Control* (FPA, 1971/14). Further information is available in the publications of the FPA and NFPA, some of which are given in Appendix 28.

The problem of fire in buildings falls under three main headings: (1) hazard to life, (2) hazard of damage to the building and (3) hazard of exposure of nearby buildings. Fire protection of buildings, as of plants, is based on a combination of passive measures such as structural design, and active ones, such as fire fighting systems.

16.36.1 Fire load

The maximum size of fire which can develop in a building depends on the amount of material available for combustion.

The severity of a fire in a building is a function of the material available for combustion. In a classic study, described below, Ingberg (1928) put forward the concept of 'fire load' as the determinant of the severity of a fire.

The fire load is the total heat which can be generated by the combustible material within the building. It is the product of the mass of material and its heat of combustion, or calorific value. The fire load density is the heat per unit area of floor which can be generated. Alternatively, the fire load density may be expressed as the equivalent mass of wood per unit area of floor. A discussion of fire load is given by Langdon-Thomas (1972).

Fire load density has been classified as follows (this table assumes a calorific value of 8000 BTU/lb for wood):

	Fire load density		*Typical occupancies*
	(lb/ft^2)	(BTU/ft^2)	
Low	12.5	$< 1 \times 10^5$	Dwellings, offices
Medium	12.5–25	$1 - 2 \times 10^5$	Factories
High	25–50	$2 - 4 \times 10^5$	Warehouses

Table 16.89 *Calorific value of some common materials (Fire Protection Association, 1971/14)*

	(kJ/kg)
Paper	15 600–18 100
Cotton	16 750
Woods	17 500–21 000
Coals	20 000–30 000
Wool	20 700
Rubber	≈40 000
Petroleum products	43 000–48 000

Langdon-Thomas comments that it is preferable to estimate the fire load density for the particular building under study. Generalized estimates are available but appear to vary widely.

The calorific values of some common materials, as given by the FPA (1971/14), are shown in Table 16.89. Further data are given in the Association National pour la Protection contre l'Incendie (1972).

16.36.2 The time–temperature curve

It has been shown that under standard conditions there is a close relationship between the time for which a building fire burns and the temperature which it attains. This was first demonstrated in 1928 by Ingberg (1928), who carried out a series of test burns in an experimental building at the National Bureau of Standards (NBS). Similar work has been done by other investigators and has led to the development of a number of standard time–temperature curves.

A standard time–temperature curve which has been widely used is that of ASTM E-119 which has changed relatively little over the years. There is also a British Standard curve, given formerly in BS 476: Part 8: 1972 and now in Part 20: 1987.

The BS 476: Part 20: 1987 curve is defined by the following equation:

$$T = 345\log_{10}(8t + 1) + 20 \qquad t \leq 360 \qquad [16.36.1]$$

where t is the time (min) and T is the temperature (°C). The ASTM E-119 curve is defined as a set of time–temperature values. These are given below together with values of the BS 476: Part 20: 1987 curve calculated from Equation 16.36.1:

Time (min)	*Temperature (°C)*	
	ASTM E119	*BS 476: Part 20: 1987*
5	538	576
10	704	678
30	843	842
60	927	945
120	1010	1049
240	1093	1153
360		1214
> 480	1260	

The ASTM and BS time–temperature curves are shown in Figure 16.128.

A fire at 900°C appears cherry red, one at 1100°C orange, and one above 1400°C white. Building fires generally look orange or yellow, which suggests a temperature in the range 1100–1200°C. This has been confirmed in practice.

The area under the time–temperature curve corresponds effectively to the fire load density. The greater

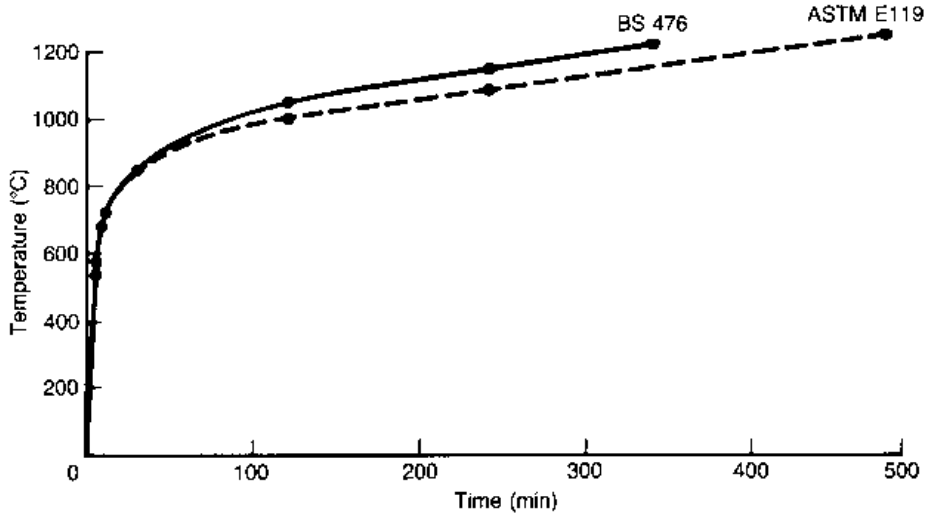


Figure 16.128 *Standard time–temperature curves for building fires. ASTM E119: 1988; BS 476: Part 20: 1987*

the fire load density, the longer the duration of the fire and the higher its temperature.

The standard time–temperature curves are widely used for the testing of structural components for fire grading. The component is put in a furnace and the temperature of the furnace is controlled to follow the curve. There is, however, a view that a test based on heat flux might be more satisfactory.

16.36.3 Fire severity

The fire load was used by Ingberg (1928) to define the severity of a potential fire. The time–temperature profile of a real fire exhibits a rapid rise to a maximum value, followed by a gentler decline. The fuel consumed is related to the area under the curve. The profile thus differs from that of a standard time–temperature curve.

The proposition put forward by Ingberg is that two fires should be regarded as of equal severity if the area under the time–temperature curve, above a certain datum temperature, is equal, a concept which has become known as the 'equal area hypothesis'.

The relationship given by Ingberg between fire load and fire severity may be expressed as:

Combustible content (kg/m^2 of wood equivalent)	*Thermal equivalent* (GJ/m^2)	*Standard fire duration* (h)
49	0.90	1
73	1.34	1.5
98	1.80	2
146	2.69	3
195	3.59	4.5
244	4.49	6
293	5.39	7.5

Here the thermal equivalent is based on the floor area and on a heat of combustion of wood of 18.4 MJ/kg.

16.36.4 Fire grading of buildings

A scheme for the fire grading of buildings in the UK which is based essentially on the concepts of fire load and the time–temperature curve was proposed in *Fire Grading of Buildings*, Part I, *General Principles and Structural Precautions* (Ministry of Works, 1946). An outline of this system is given in Table 16.90. Buildings of Types 1 and 2 have steel frames with concrete protection, brick walls and reinforced concrete or equivalent resistance floors. In Types 4 and 5 the buildings have load-bearing brick walls, timber floors and roofs, and fire-retardant roof covering; ordinary houses are of this type. A Type 6 building is made of incombustible material, such as corrugated iron or asbestos cement. A Type 7 building is one of combustible material such as wood. Although the system was never adopted as such, it illustrates some general principles of fire grading.

A different approach to fire grading is that developed by Law (1971), who investigated the relation between fire severity and fire resistance. In this work a real fire was modelled as having a temperature equal to its peak temperature maintained for a period equal to the ratio $M_f/\dot{m}$, where $\dot{m}$ is the rate of mass loss and M_f is the total mass of combustible material. Fire resistance of insulated columns was investigated using unsteady-state heat transfer models to determine the time to failure. The following relation was obtained:

$$t_f = k_f \frac{M_f}{(A_W A_T)^{\frac{1}{2}}} \qquad [16.36.2]$$

where A_T is the total area of the internal surface, excluding ventilation openings (m^2), A_W is the area of the ventilation openings (doors, windows) (m^2), M_f is the total combustible load (kg of wood equivalent), t_f is the effective fire resistance time, or fire grading (min), and k_f is a constant. With the units quoted, the value of the constant k_f is approximately unity.

Table 16.90 *Minimum fire resistance requirement for types of construction (after Ministry of Works, 1946)*

Grading of construction		*Minimum fire resistance*[a] (h)
Type 1	Incombustible fire resisting construction Fully protected in relation to high fire loads, e.g. warehouses	4
Type 2	Incombustible fire resisting construction Fully protected in relation to moderate fire loads, e.g. shops and factories	2
Type 3	Incombustible fire resisting construction Fully protected in relation to low fire loads, e.g. offices and residential buildings	1
Type 4	Fire resisting construction but not necessarily incombustible and may therefore include timber floors and timber roof construction. Partially protected only in relation to all fire loads	$\frac{1}{2}$
Type 5	Externally protected construction Fire resisting incombustible external walls, non-fire-resisting internal construction	–
Type 6	Non-fire-resisting construction Incombustible	–
Type 7	Non-fire-resisting construction Combustible	–

[a] This refers to floors and roofs and to columns and beams supporting them. Walls and columns and beams supporting them have a minimum fire resistance equal to or greater than this.

16.36.5 Fire growth in buildings

Ignition is important not only in the initiation of fire but also for its spread. After the fire has started, its growth depends on the ease with which further combustible material is ignited.

Solid materials do not have a well defined ignition temperature, but they tend to ignite at relatively low

temperatures. The ignition temperature for wood, for example, is generally taken as about 200°C. But if wood is left in contact with a hot surface such as a steam pipe for a long period, it can undergo chemical changes so that it ignites at a much lower temperature. The maximum temperature at which wood can be safely exposed for a long period has been given as 65°C (FPA 1971/14).

Once ignition has occurred, the immediate growth of the fire is affected by the form of the nearby materials. Here the surface area of the materials is important:

	Surface area (cm^2/g)
Tinder	> 20
Kindling	2–20
Bulk fuel	< 2

The fire then grows by heat transfer and flame spread.

All three heat transfer modes (convection, conduction and radiation) contribute to fire growth. Convection within the space where the fire has started is important initially; so is conduction along burning objects. As the fire grows, convection to the ceilings and conduction through the wall become significant. When the fire is well developed and temperatures are high, the contribution of radiation becomes important.

Fire spread can be considered as occurring in three ways: (1) flame spread across combustible surfaces, (2) fire spread through a continuous fuel bed and (3) fire spread through a discontinuous fuel bed.

Flame spread across a combustible surface differs somewhat according to whether it is vertical or horizontal. Spread is more rapid in the vertical direction, because the surface is preheated by convection. However, in both cases flames can spread very quickly.

Fire spread through a continuous fuel bed requires little explanation except that this description includes spread between any types of object which can act as a fuel, including whole buildings. The fuel bed is effectively continuous if the flames pass right through it.

With a discontinuous bed, by contrast, it is necessary for the fire to spread by one of the modes of heat transfer and to cause ignition by heating other objects to their ignition temperature without the aid of direct flame contact.

16.36.6 Flashover

If a fire takes hold in a compartment, a point is reached when the fire is no longer localized, but spreads throughout the whole space. There is sudden propagation of flame through the unburned gas below the ceiling and all the combustible surfaces become involved in the fire. This condition is known as 'flashover'.

In this situation the rate limiting feature frequently is no longer the fuel but the air supply. If the air supply is suddenly increased, as by the cracking of windows, the opening of a door or other means, there will be a sudden increase in the rate of burning.

With flashover, the fire is fully developed. Flashover is discussed further in Section 16.36.10.

16.36.7 Fire spread through buildings

The spread of fire through a building depends on a number of factors. Staircases, lift shafts and open corridors encourage the rapid spread of flames. Features such as gaps in walls where pipes pass through or doors left open allow flames to bypass enclosing elements which are intended to be a barrier to fire. Fire spread is also strongly influenced by the surfaces in the building. Some surfaces support a very rapid passage of flame.

16.36.8 Fire spread from buildings

Fire spread from a building across an open space is generally almost entirely by radiation, although there may sometimes be a contribution from convection and there may also be flying brands. Usually the object is heated by radiation to a temperature at which it is ignited by a small brand or spark. This is known as pilot ignition. Such pilot ignition of dry unpainted wood in the open can be obtained if the heat flux onto it is about $12.6\,kW/m^2$. A lower value is sufficient to ignite the wood in a closed room.

A method of calculating the heat radiation from the windows of a burning building has been developed by Law (1963 FRS Fire Res. Tech. Pap. 5) and has been used in conjunction with fire resistance data to determine suitable separation distances between buildings. The method is described in the original paper and in an explanatory memorandum to the Building Regulations 1965.

The amount of heat radiated from a building is a function of the area radiating heat and of the heat flux per unit area. The assumption that there is fire at all windows is a conservative one, particularly for larger buildings. The additional radiation from flames outside the windows is not generally significant.

The upper limit of the intensity of heat radiation from a fire in a room of a building can generally be taken as $168\,kW/m^2$, but a lower value applies for lower fire load densities (Langdon-Thomas, 1972).

The spread of fire between buildings depends on the distance between them, the sizes and angles of the radiating surfaces, the contents of the buildings and the construction of the buildings. The contents of the burning building determine the temperature reached and the extent to which flying brands are produced, and the materials of walls and roofs of the two buildings determine the extent to which the burning building radiates heat and produces brands and the extent to which the exposed building is vulnerable to them.

16.36.9 Effects of fire in buildings

Fire in a building presents three hazards to life: (1) toxic gas, (2) smoke and (3) heat.

People may be overcome or may be burned. Most people who die in fires do so in the early stages of the outbreak, not infrequently before the alarm has been raised. Usually they are killed by toxic gases which arrive before the fire itself reaches that part of the building. Others are overcome by toxic gas or become trapped and then die in the fire itself.

Toxic gases produced by building fires are principally the normal products of combustion, i.e. carbon monoxide and carbon dioxide. The amount of carbon monoxide produced is increased if the air supply to the fire is

limited. Carbon monoxide has almost the same density as air and so spreads easily through the building. It is odourless, and so is not readily detected. At a concentration of 1.3% it causes unconsciousness after a few breaths.

Carbon dioxide is also toxic, but in building fires acts mainly as an asphyxiant. A concentration of about 9% is generally enough to cause unconsciousness within a few minutes.

Other more toxic gases may be produced by the combustion of materials such as plastics and rubber. These include hydrogen chloride, sulphur dioxide, hydrogen cyanide and phosgene.

Smoke has the effect of reducing visibility and hindering both escape and rescue. The quantity of smoke generated is greater if the air supply is restricted and the burning material is wet.

It is often the case that smoke rising up a staircase causes people trying to escape to turn back, even though the route is actually passable. It is a prime function of fire doors, therefore, to prevent the spread of smoke. It is desirable that people in the building understand these points.

The damage done to the building by fire is due partly to the fire itself and partly to smoke and water. Some estimates of fire damage attribute more than half to water damage.

16.36.10 Modelling of building fires

Some progress has been made in the modelling of fires in buildings. Accounts of the modelling of building fires are given by Drysdale (1985), Babrauskas (1986c), Budnick and Evans (1986), Budnick and Walton (1986) and Law (1991).

Most modelling has been directed to the characterization of the fire in a compartment. There are also some models of other aspects such as fire spread along corridors. A compartment fire may (1) burn out, (2) self-extinguish due to lack of air or (3) progress to flashover.

'Flashover' has been used with a number of meanings, as reviewed by P.H. Thomas (1982). There are three in common use: (1) transition from a localized fire to a conflagration involving all the fuel surfaces in the enclosure; (2) transition from fuel to ventilation controlled burning; and (3) sudden propagation of flame through the unburnt volatiles collected under the ceiling.

The modelling of a compartment fire proceeds broadly along the following lines. The fire load in and ventilation conditions of the compartment are determined. In the pre-flashover stage, the fire is modelled first under 'free burn' conditions. As the fire grows, a transition may occur from the regime of free burning to one of ventilation controlled burning. Prior to flashover, the features of interest include (1) the fire regime, (2) the rates of mass loss and heat release, (3) the upper gas temperature and (4) the radiant heat flux.

Determination of these variables permits an estimate to be made of the possibility that flashover will occur. There are a number of criteria for flashover, which utilize (1) the upper gas temperature, (2) the radiant heat flux and (3) the heat release rate. These variables are, of course, related. The various equations involve time in some way, and hence provide a means of estimating the time to flashover, assuming that it does occur.

For the post-flashover stage, the features of interest are (1) the rates of mass loss and heat release and (2) the compartment temperature. Principal purposes of the modelling of compartment fires include determining whether flashover will occur, the time to flashover and the temperature profile after flashover.

Programmes of experimental work which have provided data for workers in the field include the Home Fire Project (Croce, 1975) and the project of the Conseil Internationale du Batiment (CIB) (Heselden and Melinek, 1975 FRS Fire Res. Note 1029).

16.36.11 Models of pre-flashover compartment fire

In the pre-flashover stage, the mass loss rate is at first relatively low. The fire regime is one of fuel controlled burning. As the fire grows, the quantity of air required increases markedly, and the regime becomes one of ventilation controlled burning.

The mass loss rate in the initial, free burning stage necessarily depends on the particular scenario, but the work of P.H. Thomas, Simms and Wraight (1964, 1965) on the modelling of crib fires provides one approach.

An equation for the mass loss rate under conditions of ventilation controlled burning has been given by Kawagoe (1958):

$$\dot{m} = k_v A_W H^{\frac{1}{2}} \qquad [16.36.3]$$

where A_W is the area of the ventilation opening (m^2), H is its height (m), $\dot{m}$ is the mass burning rate (kg/s) and k_v is a constant ($kg/m^{\frac{5}{2}}$ s). The term $A_W H^{\frac{1}{2}}$ is referred to as the 'ventilation factor'. The value given for k is 0.09, which is often rounded to 0.1. In another widely used form of the equation, $\dot{m}$ is expressed in kg/min and k_v has the value 6.

The heat release rate is

$$\dot{q} = \dot{m}\Delta H_c \qquad [16.36.4]$$

where ΔH_c is the heat of combustion (kJ/kg) and $\dot{q}$ is the heat release rate (kW).

A number of equations have been given for the estimation of the upper gas temperature in pre-flashover conditions. One is that by Quintiere (1983), quoted by Babrauskas (1986c). The temperature is a function of, among other things, the heat release rate, the ventilation conditions and time.

Another model, described by Drysdale (1985), has been given by McCaffrey, Quintiere and Harkleroad (1981).

P.H. Thomas (1974) and Ove Arup (1977) have developed a model, quoted by Budnick and Evans (1986) and Law (1991), which allows for limitation by fire load. It is

$$T_u = T_o + \frac{6000}{\eta^{\frac{1}{2}}}[1 - \exp(-0.1\eta)][1 - \exp(-0.05\tau)] \qquad [16.36.5]$$

with

$$\eta = \frac{A_T}{A_W H^{\frac{1}{2}}} \qquad [16.36.6]$$

$$\tau = \frac{L}{(A_W A_T)^{\frac{1}{2}}} \qquad [16.36.7]$$

where L is the mass of fuel (kg), η is a ventilation term ($m^{-\frac{1}{2}}$) and τ a fire load term (kg/m^2).

The radiant heat flux from the fire to the compartment boundaries is typically obtained by determining the radiative power of the flame and estimating the thermal radiation intensity as that at the surface of a hemisphere.

There are a number of criteria for flashover in a compartment fire. One takes the form of a limiting value of the upper gas temperature. Hagglund, Jansson and Onnermark (1974) and Fang (1975) obtained in their work a value of 600°C. Other workers such as Lawson and Quintiere (1985) use 500°C. Another criterion is the radiant heat flux to the floor of the compartment. Work by Waterman (1968) indicates a critical value of 20 kW/m^2. Also relevant is that in his work flashover did not occur below a mass loss rate of 40 g/s.

Since the upper gas temperature is related to the heat release rate, the flashover criterion can also be expressed in terms of a limiting heat release. One such relation, based on a flashover temperature of 600°C and enclosures with materials having a density similar to that of gypsum board, is

$$\dot{q}_{fo} = 378 A_W H^{\frac{1}{2}} + 7.8 A_T \qquad [16.36.8]$$

where $\dot{q}_{fo}$ is the heat release rate at flashover (kW). Another such equation is that by Lawson and Quintiere (1985).

16.36.12 Models of post-flashover compartment fire

Flashover results in a rapid rise in temperature, possibly up to 1100°C. There are a number of models of the post-flashover compartment fire. It is usually assumed that the atmosphere in the compartment is perfectly mixed. The models differ in two main ways. One is in the terms which are included in the heat balance. The other is in the estimation of the individual terms, and particularly the rates of mass loss and hence heat release.

Models for this stage include those by Kawagoe and Sekine (1963), Pettersson, Magnussson and Thor (1976), Babrauskas and Williamson (1978) and Babrauskas (1981). Expositions of these models have been given by Drysdale (1985) and Babrauskas (1986c).

The general nature of the models is illustrated in the account given by the latter author, who describes his own model (Babrauskas, 1981) for the post-flashover upper gas temperature in a compartment fire:

$$T_u = T_o + (T^* - T_o)\theta_1\theta_2\theta_3\theta_4\theta_5 \qquad [16.36.9]$$

where T_o is the ambient temperature (K), T_u is the upper gas temperature (K), T^* is an empirical constant, and θ_1, θ_2, θ_3, θ_4 and θ_5 are factors which allow respectively for (1) the burning rate stoichiometry, (2) the steady-state heat loss through the wall, (3) the transient heat loss through the wall, (4) the effect of the height of the opening and (5) the combustion efficiency.

A determining factor in such models is the expression used for the mass loss rate. As described above, there are two distinct regimes. At low ventilation rates the mass loss rate is ventilation controlled, whilst at high ventilation rates it is fuel controlled.

Under ventilation controlled conditions, the expression commonly used for the mass loss rate is that by Kawagoe, given above as Equation 16.36.3. The range of validity of this equation, however, is restricted. Its limitations are discussed by Drysdale. Work by Bullen (1978) points to a family of curves of the same general form as Equation 16.36.3, but with different values of the constant and hence with different slopes. In other words the group $(\dot{m}/A_W H^{\frac{1}{2}})$ is not a constant. Rather it is a function of factors such as the heat of gasification of the volatiles and the heat flux to the burning surface.

If the ventilation is increased, there comes a point at which the regime becomes fuel controlled. However, fuel control is appreciably more complex. The predominant factor is the geometry of the fuel, and above all its surface area. For this regime, therefore, there is no single criterion for transition and no single expression for the mass loss rate.

There exist methods, such as that by Harmathy (1972), for the determination of the transition from ventilation to fuel control. The application of this criterion is discussed by Drysdale, who shows that there is appreciable scatter.

In view of the variety of mass loss rates within the fuel control regime, the most widely applicable approach would appear to be to estimate the values of the mass loss rate using a correlation for each of the two regimes and to identify the transition point in this way. There is no generally applicable relation for the estimation of the mass loss rate $\dot{m}$. Bullen and Thomas (1979) have obtained a correlation which includes some of the important variables. It may be expressed as

$$\dot{m} \approx I A_f / L_v \qquad [16.36.10]$$

where A_f is the surface area of the fuel (m^2), I is the thermal radiation intensity (kW/m^2) and L_v is the heat of gasification of the volatiles (kJ/kg).

Babrauskas (1986c) treats this aspect by utilizing for both regimes expressions for the burning rate stoichiometry factor θ_1 which are a function of the ratio ϕ of the actual mass loss rate to that at stoichiometric air flow. Separate expressions are used for the fuel-rich and fuel-lean regimes, in other words for ventilation control and for fuel control.

Treatments of a fully developed compartment fire frequently use Equation 16.36.3, which is applicable to the ventilation controlled regime.

16.36.13 Models of flame projection

Flame projected from an opening may cause fire to spread to the storey above. It may impinge on an object outside and is in any event a source of radiant heat.

Flame projection has been correlated by P.H. Thomas and Law (1972) who obtained the equation

$$z + H = 12.8(\dot{m}/B)^{\frac{2}{3}} \qquad [16.36.11]$$

where

$$x/H = 0.454/n^{0.53} \qquad [16.36.12]$$

$$n = 2B/H \qquad [16.36.13]$$

where B is the width of the window (m), H is its height (m), n is a shape factor, x is the horizontal reach of the flame (m) and z is the height of the flame tip above the soffit, or top, of the window (m). Thus $(z + H)$ is the height of the flame above the base of the window.

16.36.14 Models of fire spread

The spread of fire from a compartment into other parts of a building has received less attention. Quintiere (1979) has reviewed work on this aspect.

Tests in which fires were lit in buildings due for demolition indicate that the volume of the fire tends to grow exponentially.

A particular aspect which has been studied is fire spread from a room into a corridor. Work on this has been described by Quintiere, McCaffrey and Kashiwagi (1978).

Another route for the spread of flames is through an opening and up to the next storey. Work on this indicates that such spread is influenced by the shape factor ($2B/H$), where B is the width of the opening and H is the height. For narrow windows and thus small values of this group, flame spread may occur with only a relatively small projection, whereas for wide windows a greater projection is required.

16.36.15 Models of detector response

A quite different type of fire model is that used to investigate the response of temperature measuring devices used for fire detection. An account of such models is given by Budnick and Evans (1986).

16.36.16 Models of smoke

The agent responsible for the majority of deaths in building fires is smoke. The treatment of the production and movement of smoke in such fires is therefore a significant aspect.

Smoke is produced by smouldering fires and by flaming combustion, but the types of smoke are very different. Smouldering tends to produce an oily smoke and flaming produces solid particles. Smoke generally contains unburned carbon and toxic gases. The carbon particles in smoke are the result of incomplete combustion, as is carbon monoxide. Other gases, such as hydrogen chloride or phosgene, may also be present, depending on the materials burned. Features of smoke which relevant here are that it reduces visibility and that it is toxic.

Characterization of the yield and composition of smoke is difficult due to the wide variety of materials that become involved and the range of conditions that are prevalent in fires. From the practical viewpoint, the significant feature is the rate of production of smoke, which is governed by the burning rate. The use of a suitable model for the smoke production rate permits the determination of the rate of smoke extraction required to prevent the layer of the hot smoke under the ceiling exceeding a certain depth.

One method of estimating of the rate of smoke production is to infer it from the rate of air entrainment. P.H. Thomas *et al.* (1963) have described a model based on this approach. Another model on these lines is that by Butcher and Parnell (1979).

The movement of smoke is governed by buoyancy and air movement effects. The fire itself generates hot gases and creates buoyancy effects, whilst the smoke itself has a temperature in excess of that of the atmosphere, creating a stack effect. Natural and forced ventilation are responsible for the air movement.

16.36.17 Computer models

A number of computer codes have been developed incorporating models of fires in buildings. An account is given by Budnick and Walton (1986). These computer models are of two main types: (1) enclosure fire models and (2) special purpose models.

Enclosure fire models include not only deterministic models but also probabilistic ones. A large proportion of the former are zone models in which the enclosure is divided into control volumes, or zones, and the conditions in each zone are simulated. Typically the enclosure might be divided into a lower and an upper zone. Probabilistic models deal with the transitions between different stages in the development of a fire, often using techniques such as Markov models.

There are also a number of special purpose models which address topics such as detector actuation, smoke control, structural response and evacuation.

Tabulations of the codes available are given by Budnick and Walton.

16.36.18 Fire protection by structure

The objectives of fire protection by means of the structural design of buildings are to (1) limit fire spread between buildings, (2) limit fire spread within buildings, (3) facilitate escape, (4) facilitate fire fighting and (5) limit water damage.

The Building Regulations 1976, particularly Part E, contain requirements which deal *inter alia* with: restriction of the spread of flame; provision of compartment walls and floors; fire resistance of elements of the structure, floors and doors; fire protection of penetrations, cavities and shafts; and means of escape. These requirements cover both materials and construction. Other requirements are designed to limit fire spread between buildings and deal with distances between other buildings and boundaries and with the construction and combustibility of external walls and roofs.

These regulations were revoked by the Building Regulations 1985, which are much less detailed (31 pages as opposed to 295), though they retain in Schedule 1 certain minimum requirements. The provisions of the earlier regulations retain value as an indication of good practice.

The material and component properties which are important are indicated by the tests specified in BS 476: 1970– *Fire Tests on Building Materials and Structures*. These include:

Part 3: 1975	*External Fire Exposure Roof Test*
Part 4: 1970	*Non-combustibility Test for Materials*
Part 5: 1979	*Method of Test for Ignitability*
Part 6: 1989	*Method of Test for Fire Propagation for Products*
Part 7: 1987	*Method of Classification of the Surface Spread of Flame of Products*
Part 8: 1972	*Test Methods and Criteria for the Fire Resistance of Elements of Building Construction* (obsolescent, replaced by Parts 20–23)
Part 13: 1987	*Method of Measuring the Ignitability of Products Subjected to Thermal Irradiance*
Part 20: 1987	*Method for Determination of the Fire Resistance of Elements of Construction (General Principles)*

Part 21: 1987 *Methods for Determination of the Fire Resistance of Load-bearing Elements of Construction*
Part 24: 1987 *Method for Determination of the Fire Resistance of Ventilation Ducts*
Part 32: 1987 *Guide to Full Scale Fire Tests within Buildings*

BS 476: Part 8: 1972 is obsolescent, being replaced by BS 476: Parts 20–23: 1987, which cover, respectively, (1) general principles, (2) load-bearing elements, (3) non-loading bearing elements and (4) certain special components.

The constructional features which are relevant to fire protection include:

(1) compartmental construction;
(2) fire resistance;
(3) limitation of openings;
(4) partitions and linings;
(5) roofs;
(6) vents;
(7) escape routes.

Compartments are spaces in buildings which are enclosed by fire-resistant walls and floors, and have all openings protected by fire-resistant construction. The object of compartmentation is to confine a fire to the compartment where it originates and to control the movement of flames, smoke and heat.

The maximum size of compartment is usually set by consideration of hazard to life and of ease of fire fighting. The size should be kept to a minimum consistent with the basic purpose of the building.

The fire resistance of the floors and walls should be capable of containing the most severe and prolonged fire which is likely to occur. The nature of such a fire depends on the likely contents of the compartment.

The openings between compartments should be minimal. In some explosives factories openings are virtually eliminated. But, in general, openings are acceptable, provided appropriate precautions are taken. All openings should be protected with fire-resisting doors or shutters. All vertical shafts such as staircases, lifts and hoists should have fire-resistant walls and fire-protected openings. All unnecessary openings should be closed, including those around services and pipework.

Linings for walls and ceilings should be of non-combustible material or should have low flame spread characteristics.

Roofs should be constructed so that fire does not spread either internally beneath the roof or externally over it. Flame spread beneath the roof is reduced by the use of incombustible or low flame spread materials and partitioning, and that above the roof is reduced by the use of incombustible materials and partition walls.

Vents should be provided for the release of hot gases and smoke. These control the spread of fire and smoke and assist fire fighting. The design of vents depends on the type of building.

The Building Regulations 1976, Regulation E5, specify minimum periods of fire resistance which are a function of the type and size of building and the part of the building. The required minimum periods do not exceed 2 hours, except for basements in large buildings and for large storage buildings.

16.36.19 Fire protection by sprinklers

As already mentioned in Section 16.26, the installation of fixed water sprinkler systems has proved very effective and is wholeheartedly supported by the insurance companies. Sprinkler systems for buildings are usually automatic, with a detection system which actuates the sprinklers and sounds the fire alarm.

Detection is usually based on heat or smoke. Heat sensitive detectors are dealt with in BS 5445: Part 5: 1977.

Sprinkler heads are usually arranged to cover an area not exceeding $12\,m^2$ per head. The amount of water required depends on the risk protected. For storage, for example, water requirements in the range 0.041 to $0.514\,l/m^2\,s$ have been determined, the latter being for high stacked, closely packed materials in which water penetrates with difficulty (O'Dogherty, Nash and Young, 1966).

In a large proportion of cases where a sprinkler installation has not been effective in protecting a building, this has been due to the fact that it was disabled in some way. Often the main system valve was closed. It is necessary, therefore, to have specific procedures to prevent this.

16.36.20 Smoke control

Smoke control may be applied to a space where smoke from a fire may occur and also to escape routes. Methods of smoke control include removal by venting and exclusion by maintaining a positive pressure.

The design of a smoke venting system has been treated by P.H. Thomas *et al.* (1963), P.H. Thomas and Hinckley (1964) and Butcher and Parnell (1979). Relevant factors are the height of the space, the size of the design fire, the type of roof and the pressure at the roof. A positive pressure on the roof will reduce and may negate the effectiveness of a vent. The spread of smoke under the roof may be limited by installing smoke curtains hanging down from it.

The use of smoke vents has certain drawbacks. One danger is that venting may hinder the operation of smoke detectors. Another problem is that venting of the smoke at a high level requires a compensating introduction of air at a low level, which may exacerbate the fire. Each case needs to be considered on it merits.

An escape route may be protected from smoke by the use of closed doors, by applying positive pressure and/or by venting the smoke from the space where it is being produced. Where reliance is placed on closed doors, it must be ensured by means of suitable measures, including training, that they remain closed in fire conditions. Where positive pressurization is used, air locks may be required to ensure that an adequate pressure is maintained.

16.36.21 Other fire precautions

Other fire precautions which should be taken in buildings include the following:

(1) fire alarm system;
(2) escape routes;
(3) fire fighting equipment;
(4) fire notices;
(5) fire drills.

The building should be provided with a fire alarm system which can be heard in all parts of the building and which is tested regularly. There should be clearly marked escape routes from all parts of the building. Fire fighting equipment such as portable fire extinguishers and hoses should be provided, as appropriate. The fire extinguishers used should be suitable for the types of fire which are likely to occur. Notices on the procedures to be followed should be prominently posted. Fire drills should be practised regularly.

16.37 Fire Protection in Transport

The account so far has dealt with the fire protection of fixed installations. It is also necessary to give brief consideration to fire protection, and fire fighting, in transport. The consideration here is confined to road, rail and marine transport.

In large part, the fire hazard in road, rail and marine transport is addressed by measures to prevent accidents and to ensure appropriate design and maintenance.

The principles of fighting fires arising from transport accidents are, in general, no different from those for buildings, but two aspects are of particular importance. These are the wide variety of chemicals which are carried and the relative lack of familiarity of the local authority fire services with these chemicals.

A considerable effort has been made, therefore, to furnish information to the fire services in advance about the hazards of chemicals which they may encounter. *Dangerous Substances. Guidance on Dealing with Fires and Spillages* (Home Office, 1972/4) and *Hazardous Loads* (IFE, 1972) provide some information on this aspect.

Transport aspects are discussed in more detail in Chapter 23.

16.37.1 Road transport

Accounts of fire protection and fire fighting in road transport are given in *Transportation Fire Hazards* (NFPA, 1973/10), *Hazardous Materials Response Handbook* (NFPA, 1992/30) and by Stillman (1971) and Ward (1978). Fire protection in road transport is treated in the NFPA *Handbook* by McGinley (1986).

Relevant codes for road transport are NFPA 385: 1990 *Tank Vehicles for Flammable and Combustible Liquids*, NFPA 1901: 1985 *Automotive Fire Apparatus*, NFPA 512: 1990 *Truck Fire Protection* and NFPA 513: 1990 *Motor Freight Terminals*, and, for explosive materials NFPA 495: 1992 *Explosive Materials Code* and NFPA 498: 1992 *Explosives Motor Vehicles Terminals*.

Fire fighting in road transport needs to be seen as one aspect of the wider topic of handling the emergency. With regard to fire fighting proper, principal points are prompt action in using portable extinguishers, alerting of the fire services, alerting of the public and discouragement of spectators. The fire fighting agents used should be compatible with the materials constituting the load.

Where a road tanker contains LPG, a notable hazard of a fire is that of a BLEVE.

16.37.2 Rail transport

An account of fire protection and fire fighting in rail transport is given in *Manual of Firemanship*, Book 5, *Incidents Involving Aircraft, Shipping and Railways* (Home Office, 1985). Fire protection in rail transport is treated in the NFPA *Handbook* by Fitch (1986).

Fire arrangements for rail transport are not well served with national codes, the matter tending to be left to the carrier. As with road tankers, a fire on an LPG rail tank car involves the hazard of BLEVE. The risk of such an event is much increased if there are a number of such tank cars, perhaps with a flame from the pressure relief valve of one playing on another.

16.37.3 Marine transport

Accounts of fire protection and fire fighting in marine transport are given in *Fire Aboard* (Rushbrook, 1979), *Manual of Firemanship*, Book 5 (Home Office, 1985), already referred to, and by Tanner (1976), Wynne (1986) and McKenna (1989). Fire protection in marine transport is treated in the NFPA *Handbook* by Keller, Kerlin and Loeser (1986).

Fire control is an important feature of the fighting capability of a warship. An account is given by Dimmer (1986). A relevant code is NFPA 306: 1993 *Control of Gas Hazards on Vessels*. Other codes and standards, notably the IMO codes, are detailed in Chapter 23.

The much larger storages of flammable materials in marine transport provide more scope for, and necessitate, fire protection arrangements more similar to those used in fixed installations.

Fire protection measures include the use of inerting and operational procedures to counter static electricity.

The fire protection arrangements on chemical tankers and gas carriers and the application of water sprinkler, mechanical foam, vaporizing liquid and carbon dioxide systems are discussed by Keller, Kerlin and Loeser (1986).

Another aspect of fire protection in marine transport is that relating to jetties. Accounts are given by Dicker and Ramsey (1983) and Gebhardt (1989).

Ship fire protection is considered in more detail in Chapter 23.

16.38 Fire Hazard

The types of fire typical of the process industries are those described above. The hazard of a large industrial fire may be assessed by consideration of the historical record of such fires and their effects and/or of assumed scenarios using appropriate frequency estimates and hazard and effects models.

The process industries also suffer the more common types of fire such as fires in warehouses and in buildings. Both types of fire may cause extensive damage and the latter may give rise to a high death toll.

16.38.1 Historical experience

Fire constitutes the largest proportion of major accidents involving property damage which have occurred in the process industries. However, most accidents involving large loss of life involve explosions. Frequently large fires are associated with explosions, either causing the fire or resulting from it.

A classification of fires in the process industries has been given in Section 16.1. The main headings are (1)

vapour cloud fires, (2) fireballs, (3) jet flames, (4) liquid fires, (5) solids fires, (6) warehouse fires and (7) fires associated with oxygen. These various types of fire are now considered, except for jet flames and solid fires.

In Section 16.1 vapour cloud fires are classified as: Type 1, fire with no explosion; Type 2, fire resulting from explosion; and Type 3, fire resulting in explosion.

Taking these three types of fire in turn, it is not easy to identify major fires without explosion, partly because such a fire does usually result in some explosions, notably BLEVEs, and partly because even if no explosion has occurred, this is generally not stated in the account given. Major fires on large sites therefore tend to involve explosions. Major fires on cross-country pipelines which do not involve explosions are relatively more frequent for the simple reason that targets vulnerable to a BLEVE are generally absent.

Thus a Type 1 fire occurred on an NGL pipeline at Austin, Texas, in 1973 (Case History A62). The fire engulfed and killed people in the vapour rich zone formed before ignition occurred and then burned back to the pipeline; there were six deaths.

With respect to Type 2 vapour cloud fires, such fires often occur following the explosive rupture of a vessel and release of its contents. One such fire was that at the campsite at San Carlos, Spain in 1978, described in Appendix 16, which resulted from the rupture of a passing road tanker and caused some 216 deaths.

It is common for the aftermath of a large vapour cloud explosion to involve extensive fires, particularly in the storage area of the site. Cases in point are those at refinery at Lake Charles, Louisiana, in 1967 (Case History A40) and at the chemical works at Flixborough, UK, in 1974, described in Appendix 2, which burned for 2 weeks and 1 week, respectively. The fires on Piper Alpha following the gas explosion in C Module were Type 2 fires.

An explosion characteristic of Type 2 vapour cloud fires is the BLEVE. Outstanding examples are the vapour cloud fire at Port Newark, New Jersey, 1951, in which more than 70 horizontal bullet tanks on site were destroyed (Case History A19), and that at Mexico City, Mexico, 1984, described in Appendix 4, in which the entire storage area was destroyed, with some 15 explosions being recorded over a $1\frac{1}{2}$ hour period.

Turning to fireballs, these are generally associated with the BLEVE of a vessel containing liquefied gas, but a type of fireball occurs also on oil storage tanks. A large proportion of fireballs recorded have been on transport: pipelines, road tankers and, above all, rail tank cars.

Fireballs at fixed installations include those occurring during the BLEVEs at Feyzin, France, 1966 (Case History A38), West St Paul, Minnesota, 1974, and Mexico City, Mexico, 1984, described in Appendix 4.

Fireballs on rail tank cars occurred in the BLEVEs of: propane at Crescent City, Illinois, 1970 (Case History A50); VCM at Houston, Texas, 1971 (Case History A53); propane at Kingman, Arizona, 1973 (Case History A63); and LPG at Belt, Montana, 1976. A fireball on a road tanker is exemplified by the propane fireball at Lynchburg, Virginia, 1972 (Case History A59). The radii of these fireballs have been estimated at 75–100, 150, 150, 150 and 60 m, respectively. An even larger fireball occurred on an LPG pipeline at Donnellson, Iowa, 1978, with an estimated radius of 305 m (Case History A91).

A type of liquid pool fire which figures prominently among the large losses is the tank fire. A prominent example is the fire on a 66 ft high $\times$ 256 ft diameter oil storage tank which occurred in the refinery at Milford Haven, UK, 1983 (Case History A106).

A major running liquid fire involving oil froth occurred at the refinery at Signal Hill, California, 1958 (Case History A26). The oil froth eventually covered some 27 acres, causing extensive damage and the loss of two lives. In 1970, in the refinery at Beaumont, Texas, lightning struck a 40 ft high $\times$ 60 ft diameter oil tank, causing a massive release of oil which spread to create a fire involving 16 nearby undiked tanks (Case History A46).

There have also been major running liquid fires involving LNG and LPG. The fire at Cleveland, Ohio, 1944, followed the rupture of an LNG storage tank which discharged its entire contents over the plant and the nearby urban area (Case History A12). The LNG ignited and a major fire ensued. Some of the LNG flowed as liquid down storm sewers where it mixed with air, with consequent explosions. The death toll was 128.

The release of a massive wave of liquid propane at the gas plant at Umm Said, Qatar, 1977, was, at least primarily, a liquid fire (Case History A88).

Warehouse fires constitute another category. These can involve large loss, though the death toll is usually not great. Examples are two warehouse fires in Britain, at Renfrew in 1977 (Case History A85) and at Salford in 1982, both of which involved explosions of stored sodium chlorate.

An example of a fire associated with an oxygen release is that at Brooklyn, New York, 1970, when the vessel of a road tanker ruptured violently, releasing liquid oxygen (Case History A48). A number of fires broke out as the oxygen came into contact combustible materials, and two people were killed.

There are also fires that occur during construction, maintenance and decommissioning operations. The Staten Island fire in 1973, in which 40 died, occurred in an empty LNG storage tank on which men were working (Case History A67). The tank was insulated with polyurethane foam with an aluminium–polyester lining. It was this insulation which was the main seat of the fire.

The historical record indicates that large death tolls from process fires are relatively infrequent compared with those from explosions. However, it should be emphasized that, overall, process fires are responsible for a large proportion of fatalities and damage in the process industries.

16.38.2 Hazard assessment

Hazard assessment of fire on process plant generally involves: the development of a set of scenarios for fire, principally by release and ignition, and of the associated event trees; an estimation of the frequency/probability of the initial events and of the events in the branches in the event trees from a mixture of historical data and synthesis of values; and modelling of the outcome events in the event tree, including both physical events and damage/injury.

A hazard assessment involves, in principle, the formulation of a set of scenarios and a full assessment

of the frequency and consequences of the events. An assessment which is confined either to the estimation of the frequency of the events or to the modelling of the consequences is a partial one. Hazard assessments may be generic or may relate to specific hazardous situations.

Overviews of generic process plant fire scenarios have been given for LPG by Rasbash (1979/80) and for LNG by Napier and Roopchand (1986). Essentially, the principal scenarios involve various modes of release of vapour and liquid, including rupture of pressure vessels and storage tanks and releases from pipework, hoses, pumps, and so on.

A large proportion of such releases will give rise to a vapour cloud. The assessment of this cloud involves: the modelling of cloud formation and of mixing with air during the initial release; any liquid flashing and evaporation; the dispersion of the cloud and the mass of fuel within the flammable limits; the ignition of the cloud; and the development of any overpressure. If the event gives no overpressure, it is a vapour cloud, or flash fire.

A jet, or torch, fire and an engulfing fire tend to be of interest primarily as events which may cause a vessel to suffer a BLEVE. Likewise, a fireball on a vessel are generally considered as part of the BLEVE event. Separate treatment is given to a flame on, or fireball from, a pipeline.

Some principal types of model used for the hazard assessment of fires on process plants are those for (1) vapour cloud fires, (2) fireballs, (3) jet flames, (4) pool fires (5) engulfing fires and (6) pipeline fires. Accounts of some of the models available have been given above.

An early, essentially representative, hazard assessment of fire is that given in the vulnerability model by Eisenberg, Lynch and Breeding (1975), who studied among other things the area affected by a flammable vapour cloud and the lethality of flash fires from such a cloud. The events of principal interest which they consider are marine spillages of 20 750, 83 and 0.8 t of LNG on water with drifting of the vapour cloud towards populated areas. For gas dispersion they use a modification of the Pasquill–Gifford. For ignition of the cloud they assume that an ignition source is located at the centre of each population cell and that ignition occurs if a flammable mixture reaches such an ignition source. The type of ignition source is specified for each cell by the user, the two types giving fire or explosion, respectively. For thermal injury they utilize their own probit equation, as described in Section 16.22. The populations at risk are defined in terms of the cell model already described. Some results obtained are as tabulated below:

Both explosions and flash fires are considered. The results are sensitive to the location of the population cells relative to the wind direction, so that for the cases considered the flash fire casualties for the 83 ton release were actually greater than those for the 20 750 ton one. For the 83 ton release with flash fire the effective thermal radiation intensity and time duration were 124 kW/m^2 and 0.08 min, respectively, and 58% of the people in the cell affected were killed.

The First *Canvey Report* (HSE, 1978b) included assessments of: the hazard at the specific installations at Canvey from oil spillage over the bund at storages; a vapour cloud fire from the British Gas LNG storage; and vapour cloud fires from several LPG storages. These assessments were refined in the second report (HSE, 1981a). An account of this work is given in Appendix 7.

The *Rijnmond Report* (Rijnmond Public Authority, 1982) gives hazard assessments for storages at Rijnmond of acrylonitrile, propylene and LNG. It considers vapour cloud fires, fireballs, jet flames and pool fires. An account of this work is given in Appendix 8.

The hazard assessments of BLEVEs by Drysdale and David (1979/80), Blything and Reeves (1988 SRD R488) and Selway (1988 SRD R492) include extensive treatment of fire events which could cause a BLEVE.

A general account of hazard assessment for warehouses is described by G.T. Atkinson, Jagger and Kirk (1992).

16.39 Hazard Range of Fire

The hazard range of a fire depends on the type of fire concerned. Fires other than a vapour cloud, or flash fire occur at a fixed point, and therefore the range of the fire is essentially determined by radiant heat transfer. The intensity of thermal radiation from a fire decays according to the inverse square law. For a flash fire, it is also necessary to take into account the movement of the cloud, which is likely then to be the dominant factor.

A set of relations for the hazard range of fire from LPG has been given by Considine and Grint (1985). Their treatment is based on combining models for various types of fire or flame with injury relations. The injury relations used are those of Hymes (1983 SRD R275). These give the 1% and 50% lethality levels as a function of thermal load. The relations cover flash fires, fireballs, pool fires and jet flames.

16.39.1 Vapour cloud fires

The relations given by Considine and Grint for the hazard range of a flash fire are based on their relations

LNG spillage (t)	*Wind direction towards* (°)	*Ignition*		*Fatalities*	
		Time of travel (min)	*Distance travelled* (km)	*Explosion*	*Flash fire*
20 750	50	4.2	1.01	984	
20 750	53	4.2	1.01	1238	534
83	50	5.6	1.35	921	617
83	53	No ignition			

for dense gas dispersion, which are given in Chapter 15.

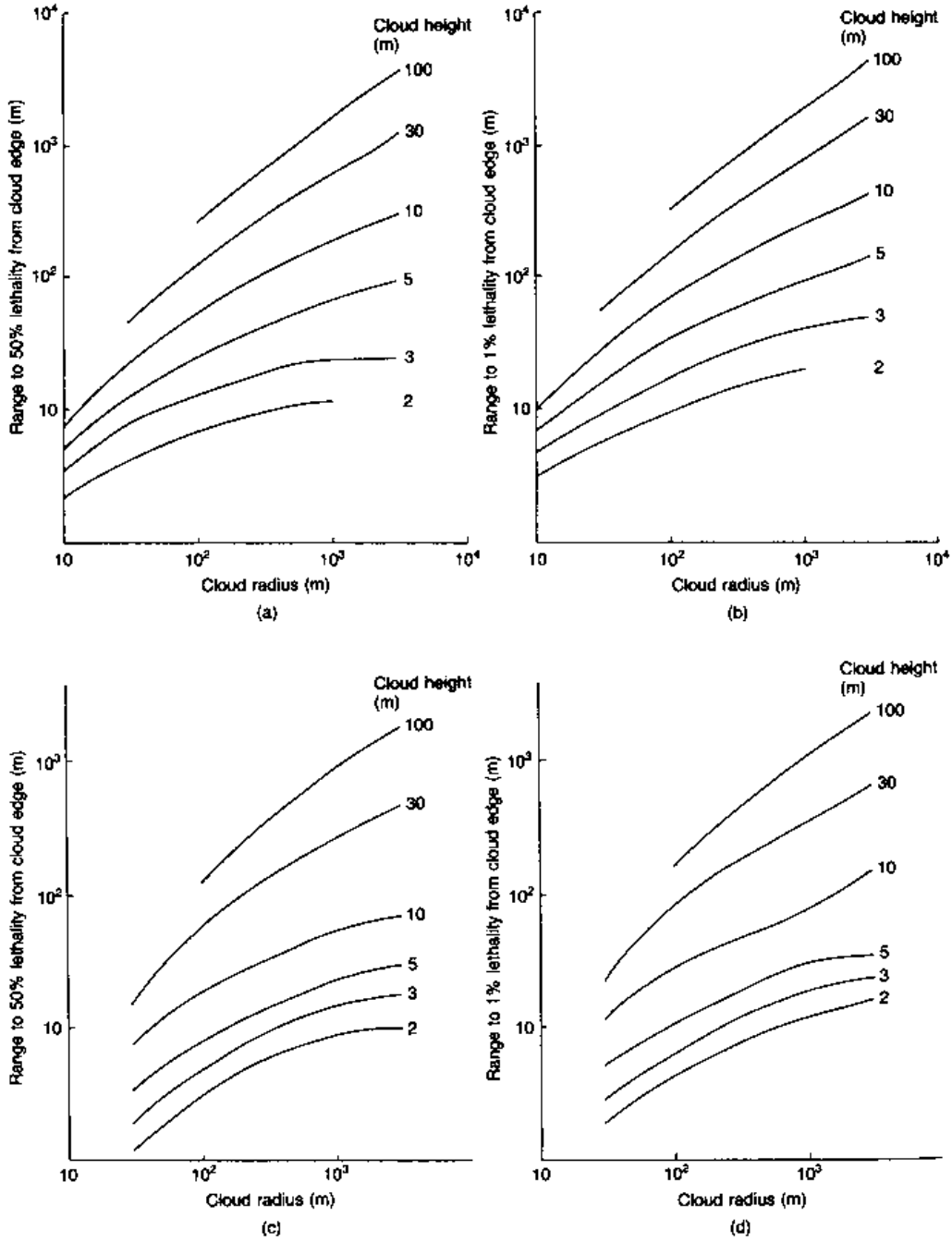


Figure 16.129 *Hazard ranges of flash fires (Considine and Grint, 1985): (a) vapour clouds with concentrations above the upper flammability limit, 50% lethality; (b) vapour clouds with concentrations above the upper flammability limit, 1% lethality; (c) vapour clouds with concentrations between the upper and lower flammability limits, 50% lethality; and (d) vapour clouds with concentrations between the upper and lower flammability limits, 1% lethality (Courtesy of Gastech)*

These are used to determine the distance to the lower flammability limit (LFL) and the flammable mass in the cloud.

The authors derive their results for a flash fire from a flash fire code in which the flame is assumed to travel radially away from the ignition source. The thermal load at a given location is then evaluated numerically. They present the results for a quasi-instantaneous release as the plots shown in Figure 16.129. Two pairs of graphs are given, one pair, those shown in Figures 16.129(a) and 16.129(b), for a cloud with concentrations between the upper flammability limit (UFL) and the LFL and another pair, shown in Figures 16.129(c) and 16.129(d) for a cloud with concentrations above the UFL. Figures 16.129(a) and 16.129(b) give the hazard ranges for 1% and 50% lethality for the first type of cloud and Figures 16.129(c) and 16.129(d) give the corresponding hazard ranges for the second type. Both types of cloud will burn: the first has the potential to give a vapour cloud explosion, whilst the second will burn by diffusion.

For a quasi-continuous release, the authors state that the envelopes for 1% and 50% lethality do not cover an area significantly different from that covered by the flammable plume and suggest that engulfment in the burning plume be taken as the basis for evaluating fatality.

16.39.2 Fireballs

For fireballs, Considine and Grint use the model of A.F. Roberts (1981/82) described in Section 16.15. The lethality relations are then

$$\left.\begin{aligned} r_{50} &= 22t^{0.379}M^{0.307} \\ r_1 &= 30t^{0.366}M^{0.306} \end{aligned}\right\} \quad 10 < M < 3000; \quad [16.39.1]$$

$$10 < t < 300; t < t_d \quad [16.39.2]$$

with

$$t_d = 4.5M^{0.33} \quad [16.39.3]$$

where M is the mass of LPG (te), r is the distance to a given lethality (m), t is the exposure time (s), t_d is the duration time (s) and subscripts 1 and 50 denote 1% and 50% lethality, respectively. The distances r are measured from the centre of the release. The maximum exposure time is limited to the duration time of the fireball.

The CCPS *QRA Guidelines* (1989/5) give the hazard distance for a fireball as

$$r_{50} = 38.9M_T^{0.432} \quad [16.39.4]$$

where M_T is the mass of fuel (ton) and r is the distance to 50% lethality (m).

Another set of hazard distances are those given for a propane fireball by Prugh (1994), as described in Section 16.22:

$$r_{50} = 38M_T^{0.46} \quad [16.39.5]$$

where M_T is the mass of fuel (ton) and r is the distance to 50% lethality (m). He draws attention to the similarity between his model and that of the CCPS.

Prugh also gives the following relations for lethal distance

$$r_{01} = 5.0W_T^{0.46} \quad [16.39.6]$$

$$r_{50} = 3.6W_T^{0.46} \quad [16.39.7]$$

$$r_{99} = 2.5W_T^{0.46} \quad [16.39.8]$$

where r is the distance to the given lethality (ft) and W_T is the mass of fuel (lb), and for second degree burns

$$r_{50} = 5.3W_T^{0.46} \quad [16.39.9]$$

and first degree burns

$$r_{50} = 3.6W_T^{0.46} \quad [16.39.10]$$

where now r is the distance to the given degree of injury (ft).

16.39.3 Pool fires

For pool fires, the model used by Considine and Grint is that by Considine (1984 SRD R297) described in Section 16.17. The treatment does not take into account flame tilt or trailing, and therefore is limited to conditions with little or no wind. Hazard range relations are given for the case of an unbunded quasi-instantaneous spill with immediate ignition and with a spreading, burning pool. The relations are

$$r_{50} = 16.1M^{0.38} \quad [16.39.11]$$

$$r_1 = 21.7M^{0.38} \quad [16.39.12]$$

The distances r are measured from the centre of the pool. The exposure time is assumed to be equal to the total burning time, and therefore does not appear explicitly in the correlations.

16.39.4 Jet flames

For jet flames of LPG, the model used by Considine and Grint is

$$L = 9.1\dot{m}^{0.5} \quad [16.39.13]$$

$$W = 0.25L \quad [16.39.14]$$

where L is the length of the flame (m), $\dot{m}$ is the mass release flow (kg/s) and W is the half-width of the flame at the flame tip (m).

Two sets of hazard range relations are given, one for persons end on and one for those side on to the flame. The end on relations are

$$\left.\begin{aligned} r_{50} &= 16t^{0.4}\dot{m}^{0.47} \\ r_1 &= 2.8t^{0.38}\dot{m}^{0.47} \end{aligned}\right\} \quad 1 < \dot{m} < 3000; \quad [16.39.15]$$

$$10 < t < 300 \quad [16.39.16]$$

where r is the distance from the edge of the flame for a given lethality (m). The side on relations are

$$\left.\begin{aligned} r_{50} &= 1.9t^{0.4}\dot{m}^{0.47} \\ r_1 &= 2.8t^{0.38}\dot{m}^{0.47} \end{aligned}\right\} \quad \begin{aligned} &1 < \dot{m} < 3000; \\ &10 < t < 300; \\ &r > W \end{aligned} \quad [16.39.17, 16.39.18]$$

where r is the distance from the axis of the flame for a given lethality (m).

16.40 Notation

Ar	Archimedes number
Bi	Biot number
Fo	Fourier number
Fr	Froude number
Le	Lewis number
Nu	Nusselt number
Re	Reynolds number
Pe	Peclet number
Pr	Prandtl number
g	acceleration due to gravity
P	absolute pressure
R	universal gas constant
t	time
T	absolute temperature
ρ	density
σ	Stefan–Boltzmann constant

Subscript:

max	maximum

Section 16.2

Sections 16.2.1–16.2.7

A	area of flame front cone; constant (Equation 16.2.12)
A'	area defined by Equation 16.2.9
B	constant
E	apparent activation energy
h	height of flame front cone
ΔH_c	net heat of combustion (kcal/mol)
k_1, k_2	constants
l	slant height of flame front cone
L	lower flammability limit (%v/v)
n	index
r	radius of flame front cone
S_u	burning velocity
t	temperature (°C)
u	velocity of gas
U	upper flammability limit (%v/v)
V	volumetric flow of gas
y	concentration of fuel component i (mole fraction)
α	half-angle of apex of flame front cone
τ	time delay before ignition

Subscripts:

i	fuel component i
t	at temperature t
25	at 25°C

Section 16.2.8

a_i	constant for component i
b_i	constant for component i
c_i	constant for component i
d_i	constant for component i
c_{pi}	specific heat at constant pressure of component i
c_{pm}	mean specific heat over range specified
c_{pmp}	mean specific heat of products
c_{pmr}	mean specific heat of reactants
ΔH_c	heat of combustion
ΔH_1	enthalpy change between states 0 and 1
ΔH_2	enthalpy change between states 1 and 2
n	number of moles per mole of fuel
p	number of products
r	number of reactants

Subscripts:

i	component i
o	standard state
p	products
r	reactants
1, 2	initial, final state

Section 16.2.9

D_o	quenching diameter
$D_\|$	critical slot width

Section 16.3

Section 16.3.3

g	boundary velocity gradient
r	diameter of tube
V	volumetric flow gas

Subscripts:

B	blow-off
F	flashback

Section 16.3.4

Equation 16.3.2:

d	diameter of pipe (m)
D	diffusion coefficient (m^2/s)
L	flame length (m)
u	fuel velocity (m/s)

Equations 16.3.3–16.3.5:

C_t	concentration of fuel in stoichiometric mixture (mold fraction)
D	diameter of pipe (m)
L	flame length (m)
M_n	molecular weight of fuel
M_s	molecular weight of surrounding fluid (normally air)
T_f	absolute adiabatic flame temperature (K)
T_n	absolute temperature of fuel in pipe (K)
W	diameter at top of flame (m)
x	axial distance (m)
Z	flame diameter (m)
α_t	ratio of number of moles of unreacted and reacted gas in stoichiometric mixture

Section 16.3.5

c_p	specific heat of gas at constant pressure
g_B	critical velocity gradient for blow-off
k	constant
K	Karlovitz number
S_u	burning velocity
T_u	absolute temperature of unburned gas
T_1	absolute temperature defined by Figure 16.17
U	flow line velocity

x, y	coordinates defined by Figure 16.17
η_o	width of wave

Equations 16.3.11–16.3.13:

d	diameter of sphere
η_o	thickness of unburnt outer shell

Subscripts:

b	burnt
u	unburnt

Section 16.3.5

A	pre-exponential factor
c	specific heat of reacting mass
E	activation energy
k	thermal conductivity
m	number defining geometry of reaction volume
Q	heat released per unit volume
Q'	heat of reaction per unit mass
r	semi-thickness or radius of reacting volume
x, y, z	distances in x, y, z directions
δ	dimensionless parameter defined by Equation 16.3.20
θ	dimensionless parameter defined by Equation 16.3.18
ζ	dimensionless parameter defined by Equation 16.3.21
τ	dimensionless parameter defined by Equation 16.3.22

Subscript:

o	initial

Section 16.3.9

c_p	specific heat of gas at constant pressure
S	burning velocity

Equations 16.3.27–16.3.29:

E	apparent activation energy
k_1, k_2	constants
p	pressure
r	radius of vessel
τ	ignition time delay

Equations 16.3.30 and 16.3.31:

d	critical diameter
h	excess enthalpy
H	minimum ignition energy
K	constant
T_f	absolute adiabatic flame temperature
T_o	absolute temperature of unburned gas mixture ahead of the flame front
ρ	density of gas mixture

Equations 16.3.32–16.3.34:

d_c	width of spark kernel
k	thermal conductivity of gas
l	characteristic flame dimension
α	thermal diffusivity of gas
δ	width of flame zone
ρ	density of gas

Subscripts:

L	laminar
T	turbulent

Equations 16.3.35 and 16.3.36:

A	constant (Equation 16.3.25)
A, B	constant (Equation 16.3.36)
E	minimum ignition energy
t	excitation time
α	index
β	index

Section 16.3.10

Equation 16.3.37:

g	acceleration due to gravity (cm/s^2)
r	radius of tube
v_o	velocity of bubble (cm/s)

Equations 16.3.38–16.3.48 and 16.3.50–16.3.52:

B	constant
m, n	indices
S_t	average velocity of displacement of turbulent wave
S_u	burning velocity
u'	axial component of turbulence
v'	radial component of turbulence
U	average velocity
y	mol fraction
α_i	ratio of mass of fuel component i + corresponding amount of oxidant to total mass of fuel + oxidant
ϕ_1, ϕ_2	functions of turbulence

Equation 16.3.40:

S_u	burning velocity (cm/s)
T_u	absolute temperature of unburned gas (K)

Subscripts:

i	component i
L	laminar
m	mixture
T	turbulent

Equation 16.3.49:

d	burner diameter (cm)
u_n	laminar burning velocity (cm/s)
u_t	turbulent burning velocity (cm/s)

Equations 16.3.53–16.3.62:

A	constant
c_p	specific heat of gas
D	diffusion coefficient of deficient reactant
k	thermal conductivity of gas
K	Karlovitz flame stretch factor
L	integral length scale of turbulence
n	index
R_L	turbulent Reynolds number
R_λ	unburnt gas Reynolds number
u'	r.m.s. turbulent velocity
u_l	laminar burning velocity
u_t	turbulent burning velocity
u_k'	effective r.m.s. turbulent velocity acting on flame
U	average velocity

λ Taylor miscoscale
ν kinematic viscosity

Section 16.3.11
A constant
c specific heat of unburned gas
d quenching diameter
d_o quenching diameter
d_p depth of penetration of quenching
d_q quenching distance
$d_{\|}$ critical slot width
f geometrical factor
g_F critical boundary velocity for flashback
k thermal conductivity of gas
k_1–k_3 constants
L gap length
S_L laminar burning velocity
S_u burning velocity
T_f absolute flame temperature
T_i absolute ignition temperature
T_o absolute temperature of unburned gas
u' r.m.s. turbulent velocity
x half-width of slot
α thermal diffusivity

Subscript:
u unburned

Section 16.3.12
c constant
k constant
m, n indices
P_{cf} absolute final pressure for cool flame
ΔP_{cf} pressure rise for cool flame
P_o initial pressure
ΔT_{cf} temperature rise for cool flame
τ ignition delay

Section 16.4

Section 16.4.2
d_L diameter of droplet
K burning constant
$\dot{m}_F$ mass burning rate of droplet

ρ_L density of liquid

Section 16.4.3
C_f flame front volumetric concentration
C_v volumetric concentration
V_a downward velocity of air
V_f upward velocity of flame through suspension
V_s sedimentation velocity of drops relative to air

Sections 16.4.4 and 16.4.5
B Spalding mass transfer number
c_p specific heat of fuel
c_{pa} specific heat of air
c_{pg} specific heat of gas
C_1 ratio of surface mean area to Sauter mean diameter
C_3 ratio of volume mean diameter to Sauter mean diameter
d_q quenching diameter
D_{32} Sauter mean diameter
E_{min} minimum ignition energy
f swelling factor of fuel
H heat of combustion
k thermal conductivity of fuel
L latent heat of vaporization
q mass ratio of fuel to air
S_g laminar burning velocity of gases liberated from particles
S_u laminar burning velocity
ΔT temperature difference

α thermal diffusivity of particle
α_g thermal diffusivity of gases
δ_r thickness of reaction zone
ϵ emissivity of particle
ρ density
ϕ equivalence ratio

Subscripts:
b boiling point of fuel
f fuel
g gas
p fuel
pr pre-reaction zone
r reaction zone
s surface of fuel
st stoichiometric

Section 16.6

a volume coefficient of expansion
A pre-exponential term
B constant (Equations 16.6.31–16.6.33 only); dimensionless parameter (Equations 16.6.86–16.6.90 only)
c specific heat of material
c_1–c_3 roots, solutions of equations
C concentration of oxygen
C_o concentration of oxygen in air
C_1, C_2 constants
d diameter of sphere
D constant
D_p diffusion coefficient in pores
E activation energy
F constant
G constant
h surface heat transfer coefficient
h_c convection heat transfer coefficient
h_r radiation heat transfer coefficient
j shape index, or factor (= 0 for slab; = 1 for cylinder; = 2 for sphere)
k thermal conductivity
M parameter defined by Equation 16.6.108
n index
P parameter defined by Equation 16.6.109
q heat transferred by radiation
Q heat released by reaction per unit volume
$Q(T_a)$ modified heat released by reaction per unit volume
Q' heat released by reaction per unit mass
Q'' modified heat released by reaction per unit volume
Q^* modified heat released by reaction per unit mass

r	radial distance, half-width
r_1	inner radius of cylinder
r_2	outer radius of cylinder
R	gas constant
R_o	average radius
S	surface area
t	time
T	temperature
ΔT	temperature difference
V	volume
x	horizontal distance
z	dimensionless distance
α	Biot number
β	effective heat transfer coefficient
δ	dimensionless ignition parameter
δ_c	critical ignition parameter
δ^*	modified critical ignition parameter
ϵ	dimensionless parameter
ϵ_1	emissivity of surface
ϵ_2	emissivity of surroundings
θ	dimensionless temperature difference
ν	kinematic viscosity
ρ	density of material
τ	dimensionless time
ξ	dimensionless parameter defined by Equation 16.6.78
χ	dimensionless parameter defined by Equation 16.6.93
ϕ	fractional conversion
ϕ^*	small fractional conversion necessary to initiate autocatalytic reaction
ψ	fractional temperature defined by Equation 16.6.100
$\psi(C)$	concentration function defined by Equation 16.6.80
ψ'	derivative of ψ with respect to τ
ω	dimensionless concentration

Subscripts:

a	ambient
c	critical value
cb	critical value for cube
f	fluid
i	induction, initial value
im	initial value for medium
o	centre
p	hot face
s	surface
sb	critical value for slab

Section 16.7

a	radius of sphere (m); half distance between axes of two parallel cylinders (m) (Equation 16.7.53 only); length of tank (m) (Equations 16.7.184–16.7.187, 16.7.190 and 16.7.191 only)
A	area (m^2)
A_n	parameter defined by Equation 16.7.185
A_p	cross-sectional area of pipe (m^2)
b	radius of sphere (m); width of tank (m) (Equations 16.7.184–16.7.187, 16.7.190 and 16.7.191 only)
B	parameter defined by Equation 16.7.65; parameter defined by Equation 16.7.185
c	concentration of ions ($kmol/m^3$); height of tank (m) (Equations 16.7.184–16.7.187 only)
c	constant
c_o	concentration of ions in the bulk fluid ($kmol/m^3$)
c_s	concentration of ions at the pipe wall ($kmol/m^3$)
c^*	charging tendency (As/m^2)
C	capacitance (F)
d	diameter (m)
d_d	diameter of droplet, particle (m)
d_p	diameter of pipe (m)
D	displacement (C/m^2)
D_m	molecular diffusion coefficient (m^2/s)
e	charge on proton (C) ($= 1.6 \times 10^{-19}$)
E	field strength (V/m)
E_b	breakdown field strength (V/m)
E_e	field strength for onset of incendive discharge (V/m)
E_i	field strength at surface of inner cylinder (V/m)
E_{mf}	maximum field strength with tank full of liquid (V/m)
E_{mh}	maximum field strength with tank half full of liquid (V/m)
E_o	field strength at surface of outer cylinder (V/m)
E_v	field strength in vapour space of tank (V/m)
E_z	field strength at distance z below roof of tank (V/m)
E_γ	field strength at fraction γ of tank height (V/m)
f	friction factor
f	fraction of charge unrelaxed (Equations 16.7.161–16.7.162 only)
F	Faraday's constant (C/kmol) ($= 9.65 \times 10^7$)
F_c	field applied in contact between surfaces (N)
F_e	force (VAs/m)
g	acceleration due to gravity (m/s^2)
G	parameter defined by Equation 16.7.142; conductance (S) (Equation [16.7.3] only)
h	height of liquid in tank (m)
h_l	height of liquid in tank (m)
h_v	height of vapour in tank (m)
H	height of tank (m)
I	current (A)
I_i	current at inlet of pipe (A)
I_{lk}	leakage current (A)
I_o	current at outlet of pipe, at inlet of tank (A)
I_∞	streaming current in infinitely long pipe (A)
j	charge flux (A/m^2)
J	current density (A/m^2)
k	Boltzmann constant (J/K) ($= 1.38 \times 10^{-23}$); constant (Equation 16.7.221 only)
l	length (m)
L	length of tank (m)
m	mass (kg)
n	number of ions per unit volume ($ions/m^3$)
n_d	number of droplets per unit volume ($droplets/m^3$)
n_t	transference number

N	Avogadro's constant (molecules/kmol) ($= 6.02 \times 10^{26}$)
p	height of vapour space (m)
P	pressure (N/m^2)
ΔP	pressure drop (N/m^2)
q	charge (C)
q'	charge (on second body) (C)
q_o	charge in equilibrium with initial voltage (C) (charging); initial charge (C) (discharging)
Q	volumetric flow (m^3/s)
r	radial distance (m); (with subscript) radius (m)
r_c	radius of cylinder (m)
r_i	radius of inner cylinder (m)
r_o	radius of outer cylinder (m)
r_p	radius of pipe (m)
R	universal gas constant (VC/mol K)
R	resistance (Ω); gas constant (Equations 16.7.103–16.7.106 and 16.7.133–16.7.136 only)
R_p	resistance of liquid in pipe (Ω)
s	space charge density (C/m^3)
s_m	mass charge density (C/kg)
s_{mf}	space charge density with tank half full of liquid (C/m^3)
s_{ms}	space charge density with tank full of mist (C/m^3)
s_o	space charge density of liquid entering tank (C/m^3); initial space charge density (Equation 16.6.202 only) (C/m^3)
s_t	space charge density of liquid in tank (C/m^3)
S	surface area (m^2)
t	time (s)
$t_{\frac{1}{2}}$	half-life (s)
T	absolute temperature (K)
u	liquid velocity (m/s); ionic mobility (m^2/V s) (Equations 16.7.85–16.7.113)
u_{st}	Stokes' velocity (m/s)
v	ionic velocity (m/s)
V	potential difference, potential above earth, voltage (V)
V_{cn}	volume of containment (m^3)
V_d	potential difference across double layer (V)
V_e	volume of charge cloud (m^3)
V_o	initial voltage (V)
V_s	streaming potential (V)
V_{set}	settling potential gradient (V/m)
V_{ves}	volume of vessel (m^3)
w	fraction of height of tank filled with liquid
W	energy, work (J)
x	distance (m); half-distance between parallel plates (m) (Equation 16.7.56 only)
x, y, z	spatial coordinates (m)
X	volume fraction of dispersed phase (v/v)
Y	parameter defined by Equation 16.7.148
z	number of elementary charges per particle
α	shape parameter defined by Equation 16.7.186; parameter defined by Equation 16.7.169
β	shape parameter defined by Equation 16.7.152; parameter defined by Equation 16.7.187; parameter defined by Equation 16.7.191
γ	surface tension (N/m); fraction of tank height at which field strength is measured (Equation 16.7.184 only)
δ	thickness of double layer (m)
δ_m	thickness of diffusion layer (m)
ϵ	relative permittivity, dielectric constant
ϵ_a	absolute permittivity (F/m)
ϵ_{ar}	relative permittivity of air
ϵ_o	permittivity of free space (F/m) ($= 8.85 \times 10^{-12}$)
η	viscosity (kg/m s)
ζ	zeta potential (V)
κ	conductivity (S/m $= \Omega^{-1}$ m^{-1})
κ_e	effective conductivity (S/m)
κ_r	rest conductivity (S/m)
λ	parameter defined by Equation [16.7.160]
ν	kinematic viscosity (m^2/s)
ρ	volume resistivity, resistivity (Ω m)
ρ_e	effective density of dust cloud or settled powder (kg/m^3)
ρ_l	density of liquid (kg/m^3)
ρ_s	density of particle material (kg/m^3)
$\Delta\rho$	density difference between droplet and continuous liquid phase (kg/m^3)
σ	surface charge density (C/m^2)
τ	relaxation time, relaxation time constant (s)
τ_o	initial relaxation time (s)
τ_s	shear stress (N/m^2)
τ_{so}	shear stress at wall (N/m^2)
ϕ	potential (V)
ψ	Euler's constant ($= 0.577$)

Subscripts:

d	droplet, particle
fp	fill pipe
l	liquid
lk	leakage
ms	mist
p	pipe
t	tank
v	vapour
ves	vessel
∞	infinitely long pipe

Units:

Units in this section are SI, as given above, with the following exceptions:

Equations 16.7.123–16.7.150, 16.7.152, 16.7.154–16.7.156: cgs units.

Sections 16.7.34 and 16.7.36: units defined locally.

For resistivity:

ohm^{-1} $= \Omega^{-1}$ = mho = S.

Units of surface resistivity: Ω.

Units of volume resistivity: Ω m.

cu = conductivity units (pS/m)

Section 16.10

P	probability of ignition
P_a	probability of ignition by event itself
P_b	probability of ignition by a specific ignition source
$P_{b,i}$	probability of ignition by a ignition source i
$P_{b,i,1}$	probability that ignition source i is present
$P_{b,i,2}$	probability that flammable region of gas cloud reaches ignition source i

$P_{b,i,3}$ probability that ignition source i if active is able to ignite gas
$P_{b,i,4}$ probability that ignition source i is active
P_c probability of ignition by a background ignition source
r distance
θ direction
θ_s semi angle of sector
μ density of ignition sources

Subscript:
i ith ignition source

Section 16.11

B rate of penetration of burning into fuel bed
C mass of air required for complete combustion of unit mass of fuel
d depth of fuel bed consumed by fire
D duct diameter
f fraction of surface covered by lining
L length of flame zone
L^* dimensionless parameter defined by Equation 16.11.1
V velocity of advance of leading edge of flame
V^* dimensionless parameter defined by Equation 16.11.2
V_A velocity of air
ρ_A density of air
ρ_f density of fuel bed

Section 16.13

A area
A constant in Equation 16.13.59
A_i constant in Equation 16.13.55a
B radiosity
c velocity of sound
c_o velocity of sound in vacuum
C_c correction factor for emissivity of carbon dioxide
C_w correction factor for emissivity of water vapour
e emissive power
F_A angle factor
$F_{A_1-A_2}$ angle factor between surface A_1 and surface A_2
F_o interchange factor
F_ϵ emissivity factor
h Planck's constant
H incident radiation
i intensity of radiation
I intensity of radiation
I_o intensity of radiation at surface of source
J_T thermal radiation flux (unattenuated)
k Boltzmann constant
k_i constant in Equation 16.13.55
k_1, k_2 constants in Equation 16.13.52
L mean path length
n refractive index
P_{CO_2} partial pressure of carbon dioxide
P_{H_2O} partial pressure of water vapour
r distance
R radiant heat factor
V visual range
w concentration of water in atmosphere (pr mm) (pr = precipitative water; see text)
w_i concentration of water in atmosphere which causes absorption in window i to go from weak band to strong band absorption (pr mm)
x path length in flame
X path length outside flame
α absorptivity
β extinction coefficient
β_i constant in Equation 16.13.55b
γ scattering coefficient
ϵ_{CO_2} emissivity of carbon dioxide
ϵ_{H_2O} emissivity of water vapour
$\Delta\epsilon$ emissivity correction
Φ radiant heat flux
θ angle
κ absorption coefficient
λ wavelength
ν wave frequency
ρ reflectivity
τ transmissivity
τ_{ai} transmissivity based on absorption in window i
τ_{si} transmissivity based on scattering in window i
τ_{Ti} total transmissivity in window i
ω solid angle

Subscripts:
b black body
i, j for surfaces i, j
s source
t target
λ for wavelength λ
ν for wave frequency ν

Section 16.14

Section 16.14.5
A_r area of radiation of hot gas layer (m^2)
c_p specific heat of hot gas layer (J/kg K)
I_r effective thermal radiation intensity (W/m^2)
k parameter defined by Equation 16.14.9
k_l concentration at lower explosive limit (kg/m^3)
k_u concentration at upper explosive limit (kg/m^3)
m total mass of vapour released
q heat loss by radiation (W)
r_l parameter of cloud at lower explosive limit
r_u parameter of cloud at lower explosive limit
t time (s)
t_{eff} effective duration of fire (s)
$t_{\frac{1}{2}}$ half-life of fire (s)
T_a absolute temperature of environment (K)
T_g absolute temperature of hot gas (K)
V_r volume of hot gas layer (m^3)
x, y, z distance in downwind, crosswind, vertical directions (m)
β parameter defined by Equation 16.14.13
ϵ_a emissivity of environment
ϵ_g emissivity of hot gas
ρ density of hot gas layer (kg/m^3)
σ Stefan–Boltzmann constant ($W/m^2 K^4$)

σ_x, σ_y, σ_z dispersion coefficients in downwind, crosswind, vertical directions (m)

Subscripts:
i initial

Sections 16.14.6 and 16.14.7
D cloud depth (m)
H visible flame height (m)
r stoichiometric air–fuel mass ratio
S flame speed (m/s)
U_w wind speed (m/s)
w parameter
W width of pool fire
α constant pressure expansion ratio for stoichiometric combustion
ρ_a density of air (kg/m^3)
ρ_o density of fuel–air mixture (kg/m^3)
ϕ volumetric concentration of fuel (v/v)

Subscript:
st stoichiometric

Section 16.15

Sections 16.15.5–16.15.9
D diameter of fireball (m)
f fraction of fuel released entering fireball
k_1, k_2 constants
M mass of fuel (kg)
M_r mass of liquid released (kg)
n_1, n_2 indices
t_a duration of combustion in system dominated by initial momentum effects (s)
t_b duration of combustion in system dominated by buoyancy effects (s)
t_c duration of combustion in system dominated by deflagration effects (s)
t_d duration time of fireball (s)
t_e time at which lift-off occurs (s)

ϕ fraction of liquid vaporized

Equation 16.15.9a:
d persistence time (s)
W mass of propellant (lb)

Equation 16.15.15:
P absolute pressure at moment of release (MPa)

Equation 16.15.16:
E surface emissive power (kW/m^2)
P absolute pressure (MPa)

Sections 16.15.11–16.15.13
E surface emissive power
F view factor
h height of centre of fireball
ΔH_c heat of combustion (kJ/kg)
I heat received by target
l distance between centre of fireball and target
Q heat release rate (kW)
Q_r heat radiated
r radius of fireball
x distance from point directly beneath centre of fireball and target, or ground distance

α absorptivity of target
τ atmospheric transmissivity
θ, ϕ angles defined in Figure 16.87

Section 16.15.15
F_B buoyancy force (N/m^2)
F_R fluid resistance force (N/m^2)
g acceleration due to gravity (m/s^2)
r radius of fireball (m)
t time (s)
t_b burnout time

ρ density of fireball (kg/m^3)

Equations 16.15.33–16.15.40:
r radius of fireball (ft)
r_b radius of fireball at burnout (ft)
R rate of addition of propellant (lb/s)
t time (s)
W mass of fireball (lb)
W_b mass of propellant, and fireball, at burnout (lb)
ρ_b density of fireball at burnout (lb/ft^3)

Subscript:
b burnout

Section 16.15.16
D diameter of fireball (m)
M mass of fuel (kg)
r radius of fireball (m)
t_b duration time of fireball (s)
W_b mass of fireball, including air, at burnout (kg)
W_f mass of fuel (kg)

Section 16.15.17
r radius of cloud
t time
V_f volume of initial cloud of fuel
z height of centre of cloud

β entrainment coefficient
ρ_a density of air
ϕ equivalence ratio

Subscripts:
p products
r reactants

Section 16.15.18
M mass of fuel
t_b burning time
v_o mean release velocity

ρ_a density of air

Section 16.15.19
c specific heat (kJ/kg °C)
D diameter of fireball (m)
f flash fraction

F_r fraction of heat radiated, heat radiation factor
g acceleration due to gravity (m/s^2)
H enthalpy of fireball (kJ)
ΔH_c heat of combustion (kJ/kg)
I heat radiation intensity received by target (kW/m^2)
l distance from centre of fireball to target (m)
M mass of fuel released (kg)
M_a mass of air in fireball (kg)
M_f mass of fuel in fireball (kg)
N parameter governing transition from control by momentum to control by gravity slumping
P vapour pressure (MPa)
Q heat of combustion (kJ/kg)
Q_r heat radiation rate (kW)
r radius of cloud (m)
R stoichiometric value of M_a/M_f
t time (s)
t' time for cloud to fall below lower flammability limit (s)
t_d duration time of fireball (s)
t_e lift-off time (s)
t_g time to transition from control by momentum to control by gravity slumping (s)
T_f absolute mean temperature of fireball (K)
T_o absolute temperature of initial reactants (K)
V volume of cloud (m^3)

α momentum per unit mass (m/s)
η thermal efficiency
$\Delta\rho$ density difference between vapour and air (kg/m^3)
ρ_a density of air (kg/m^3)
ρ_f density of products at temperature T_f (kg/m^3)
ρ_o density of products at temperature T_o (kg/m^3)
ρ_v density of vapour (kg/m^3)

Section 16.15.20
D_{FB} duration time of fireball (s)
E_T heat released (J)
F_R fraction of heat radiated
H heat of combustion (J/kg)
I_T unattenuated thermal radiation at radius of target (W/m^2)
I_{TA} thermal radiation at radius of target, taking account of atmospheric attenuation (W/m^2)
M mass of fuel in fireball (te)
M_s mass of fuel in vessel (te)
P_D radiative power density (W/m^3)
P_{FB} radiative power (W)
R_{FB} radius of fireball (m)
R_T distance from centre of fireball to target (m)
T_e effective absolute fireball temperature (K)
V_{FB} volume of fireball (m^3)
X parameter

σ Stefan–Boltzmann constant (W/m^2K^4)
τ atmospheric transmissivity
ϕ theoretical adiabatic flash fraction

Section 16.16

Sections 16.16.4 and 16.16.5
D diameter of fireball (m)
M mass of chemicals (kg)
t_d duration time of fireball (s)

Section 16.16.6
d diameter of fireball (ft)
D diameter of fireball (m)
M mass of material (fuel + oxidizer) in fireball (kg)
t_d duration time of fireball (s)
W mass of material (fuel + oxidizer) in fireball (lb)

Section 16.16.7
d diameter of fireball (ft)
D diameter of fireball (m)
M mass of explosive (kg)
t_d duration time of fireball (s)
W mass of explosive (lb)

Section 16.16.9
D diameter of fireball (m)
M mass of explosive (kg)
t_c time to complete combustion (s)
t_d duration time of fireball (s)
t_s time for transition from hemispherical to spherical shape (s)
T_f absolute temperature of fireball at termination

ϕ parameter defined by Equation 16.16.21

Section 16.17

Section 16.17.4
d pan diameter
u velocity
v liquid burning velocity

μ viscosity
ρ density

Subscripts:
g gas
l liquid

Section 16.17.5
c_p specific heat of air (kJ/kg)
D flame diameter (m)
D' elongated flame base (m)
D_w maximum pool dimension in direction of wind (m)
g acceleration due to gravity (m/s^2)
ΔH_c heat of combustion of fuel (kJ/kg)
L flame height (m)
m mass burning rate (kg/m^2s)
N dimensionless parameter defined by Equation [16.17.4]
Q total heat release rate (kW)
r_s stoichiometric mass air to volatiles ratio
T_o absolute temperature of ambient air (K)
u wind speed (m/s)
u^* dimensionless wind speed
u_c characteristic wind speed (m/s)

u_{10} wind speed at height of 10 m (m/s)
u_{10^*} dimensionless wind speed at height of 10 m
α, β, γ number of carbon, hydrogen, oxygen atoms in fuel molecule
θ angle of tilt from vertical (rad)
μ_a viscosity of air (kg/m s)
ρ_a density of ambient air (kg/m^3)
ρ_g density of fuel vapour at normal boiling point (kg/m^3)

Equations 16.17.5 and 16.17.6:
A constant
u vapour velocity (m/s)
ρ density of vapour (kg/m^3)
$\Delta\rho$ density difference between vapour and air (kg/m^3)

Section 16.17.6
d pool diameter
F view factor
k extinction coefficient
q heat transferred from flame to pool
q_c heat transferred from flame to pool by conduction
q_r heat transferred from flame to pool by radiation
q_{rim} heat transferred from flame to pool by pan rim
T_b absolute temperature of burning liquid surface
T_r absolute temperature of flame
U heat transfer coefficient

Equations 16.17.27 and 16.17.28:
ΔH_c net heat of combustion (kJ/kmol)
ΔH_v latent heat of vaporization (kJ/kmol)
k_1, k_2 constants
v liquid burning rate (cm/min)
v_∞ liquid burning rate for pool of infinite diameter (cm/min)

Equations 16.17.29 and 16.17.30:
m mass burning rate (kg/m^2 s)
m_∞ mass liquid burning rate for pool of infinite diameter (kg/m^2 s)
ϵ flame emissivity
ρ_l density of liquid (kg/m^3)

Equations 16.17.31–16.17.39:
Δh_g total heat of gasification (kJ/kg)
k absorption–extinction coefficient
k_3 constant
L_m mean beam length
m mass burning rate (kg/m^2 s)
m_∞ mass liquid burning rate for pool of infinite diameter (kg/m^2 s)
T_f absolute temperature of effective equivalent gray gas (K)
β mean beam length corrector
ϵ flame emissivity

Section 16.17.8
Equation 16.17.40:
d diameter of fire (ft)
k_4 constant
q heat flux from surface (BTU/ft^2 h)
q_∞ heat flux from surface of 'large' fire (BTU/ft^2 h)

Equation 16.17.41:
E surface emissive power (kW/m^2)
T_f absolute temperature of flame (K)
ϵ emissivity of flame

Section 16.17.9
A, B parameters defined by Equations 16.17.46c and 16.17.46d, respectively
A_1–A_4 parameters defined by Equations 16.17.51d, 16.17.51f, 16.17.51h and 16.17.51i, respectively
B_1 parameter defined by Equation 16.17.51e
E surface emissive power (kW/m^2)
$f(v)$ parameter defined by Equation 16.17.51g
F view factor
h height of tank
I heat radiation incident on target (kW/m^2)
l, l' distances defined by Figures 16.94, 95 and 97
l_s slant distance between heat source and target
L parameter defined by Equations 16.17.46a, 16.17.48b, 16.17.51a, 16.17.58b
Q_r heat radiation rate (kW)
r radius of surface (m)
R parameter defined by Equations 16.17.44a and 16.17.56a
x ground distance between source and target (m)
X parameter defined by Equations 16.17.46b, 16.17.48c and 16.17.51b

α absorptivity
β angle of target surface to horizontal
θ angle of tilt of cylinder
τ atmospheric transmissivity
ϕ parameter defined by Equation 16.17.51c

Subscripts:
h horizontal surface
m maximum
v vertical surface

Section 16.17.13
D diameter of cylinder
F view factor
h height of flame (m)
Δh_c heat of combustion (kJ/kg)
H dimensionless flame height
k extinction coefficient
l distance from centre of flame to target (m)
L dimensionless distance to target
m mass burning rate (kg/m^{2}s)
P radiative power (kW)
q_i thermal radiation incident on target (kW/m^2)
T_f absolute temperature of flame (K)

β mean beam length corrector
ϵ_f emissivity of flame
χ_r fraction of heat radiated

Subscript:
∞ pool of infinite diameter

Section 16.17.15
Fr' modified Froude number
g acceleration due to gravity (m/s^2)
H length of flame (m)
u_w wind speed (m/s)
W width of trench (m)
W' extended width of flame base (m)

θ angle of tilt of flame (°)

Section 16.18

Sections 16.18.2–16.18.4
C_L lower explosive limit (v/v)
$\bar{C}_L$ modified lower explosive limit (v/v)
d flare diameter (m)
D distance from centre of flame to target (m)
F_r fraction of heat radiated
I heat radiation intensity incident on target (kW/m^2)
k ratio of specific heats of gas
K allowable heat radiation incident on target (kW/m^2)
M molecular weight of gas
P pressure just inside flare tip (kPa)
Q net heat release rate (kW)
r radius from centre of flame (m)
R parameter defined by Equation 16.18.10
T absolute temperature of gas (K)
u_j exit velocity of gas at flare tip (m/s)
u_s velocity of sound (m/s)
u_∞ wind velocity (m/s)
V volumetric flow of gas (m^3/s)
W mass flow of gas (kg/s)
$\Sigma\Delta x$ horizontal deviation of flame (m)
x_c horizontal distance from flare tip to centre of flame (m)
$\Sigma\Delta y$ vertical deviation of flame (m)
y_c vertical distance from flare tip to centre of flame (m)

τ atmospheric transmissivity

Subscript:
j flare tip

Section 16.18.6
A surface area of flame (m^2)
b lift-off distance of flame frustrum (m)
C parameter defined by Equation 16.18.30
d_j diameter of virtual source (m)
d_o throat diameter of imagined flow nozzle (m)
D_s effective diameter of source (m)
E surface emissive power (kW/m^2)
F view factor
F_r fraction of heat radiated
g acceleration due to gravity (m/s^2)
I heat radiation incident on target (kW/m^2)
K parameter defined by Equation 16.18.25
L_B length of flame (m)
L_{Bo} length of flame in still air (m)
$\dot{m}$ mass flow of gas (kg/s)
M molecular weight
M_k kilogram molecular weight of gas (kg/mol)
P_o atmospheric pressure (N/m^2)
Q neat heat release rate (kW)
R velocity ratio
R_c gas constant (J/mol K)
R_L length of flame frustrum (m)
T absolute temperature (K)
T_j absolute temperature of gas in expanded jet (K)
W mass fraction of fuel in stoichiometric mixture with air
W_1 width of base of flame frustrum (m)
W_2 width of top of flame frustrum (m)
u gas velocity (m/s)
u_j velocity of gas in expanded jet (m/s)
v wind velocity (m/s)

α angle between hole axis and flame axis (°)
α_b angle between hole axis and line joining tip of flame to centre of hole plane (°)
β parameter defined by Equation 16.18.19
γ ratio of gas specific heats
θ_j angle of flame to horizontal (°)
θ_{jv} angle between hole axis and wind vector in plane containing hole axis, flame axis and wind vector (°)
ρ_a density of air (kg/m^3)
ρ_{g^o} density of gas at standard conditions (kg/m^3)
ρ_j density of gas in expanded jet (kg/m^3)
ξ Richardson number based on flame length in still air
τ atmospheric transmissivity
Ψ parameter defined by Equation 16.18.17

Subscripts:
a air
j expanded jet
p mean product value
l adiabatic combustion conditions

Section 16.18.7
A total surface area of flame (m^2)
b lift-off distance (m)
$c(\xi)$ parameter defined by Equation 16.18.49
d_j diameter of expanded jet (m)
D_s effective source diameter (m)
$f(\xi)$ diameter defined by Equation 16.18.45
F view factor
$F_{s\infty}$ fraction of heat radiated for flames which emit black body radiation
g acceleration due to gravity (m/s^2)
G initial momentum flux of expanded jet (N)
$h(\xi)$ parameter defined by Equation 16.18.48
k gray gas absorption coefficient (m^{-1})
L characteristic length (m) (Equation 16.18.38:); length representing emitting path length (Equation 16.18.55)
Lb_{xy} parameter defined by Equation 16.18.51
L_{bo} length of vertical flame in still air (m)
q heat radiation incident on target (kW/m^2)
Q net heat release rate (kW)
$r(\xi)$ parameter defined by Equation 16.18.46

S surface emissive power (kW/m^2)
S_∞ black body surface emissive power (kW/m^2)
u_a wind speed in release direction (m/s)
u_j velocity of expanded jet (m/s)
w_a wind speed perpendicular to release (m/s)
W mass fraction of fuel in stoichiometric mixture with air
W_1 maximum diameter of flame (m)
W_2 minimum diameter of flame (m)
x, y, z distances in release, vertical, crosswind directions (m)
X, Y, Z x, y, z positions of flame

ρ_a density of air (kg/m^3)
ρ_j density of expanded jet (kg/m^3)
τ atmospheric transmissivity
ξ Richardson number
Ψ parameter defined by Equation 16.18.40
Ω_x, Ω_y parameters defined by Equations 16.18.42 and 16.18.43

Subscripts:
a air
en end of flame
j expanded jet
sd side of flame

Section 16.19

Section 16.19.2
l_i impingement distance (m)
m mass flow (kg/s)

Section 16.19.6
D_{max} maximum cone diameter (m)
F_x, F_y, F_z view factors defined by Equations 16.19.3, 16.19.4 and 16.19.6
h height of vent orifice (m)
h_1 distance from ground to bottom of flame radiator (m)
h_2 distance from ground to top of flame radiator (m)
I radiant heat flux (W/m^2)
l length of flame (m)
r radius of flame at tip (M)
T absolute temperature of flame (K)
x, y distances defined in Figure 16.106 (m)

ϵ emissivity of flame

Section 16.19.7
A, B, C constants
d diameter of orifice (m)
D diameter of flame (m)
F fraction of heat radiated
g acceleration due to gravity (m/s^2)
h lift-off height (m)
H height of flame (m)
H^* flame radiation height (m)
m index
Q heat release rate (MW)
u gas velocity at nozzle exit (m/s)

Section 16.19.9
D_j diameter of jet (m)
ΔH_c heat of combustion (J/kg)
L length of flame (m)
$\dot{m}$ mass flow (kg/s)
R_s radius of flame at distance s (m)
s distance along centre line (m)
u_j velocity of jet (m/s)
u_w wind velocity (m/s)
x, z distances in horizontal, vertical directions (m)

Section 16.19.10
F fraction of heat radiated
ΔH_c heat of combustion (kJ/kg)
$\dot{m}$ mass flow (kg/s)
q heat radiation incident on target (kW/m^2)
x distance from source to target (m)

τ atmospheric transmissivity

Section 16.19.11
L flame length (m)
q fuel flow (kg/s)

Section 16.19.2
L length of flame (m)
$\dot{m}$ mass flow (kg/s)
W half-width of flame at tip (m)

Section 16.19.13
f fraction of heat radiated
F flame length (m)
H_c heat of combustion (J/kg)
m mass flow (kg/s)
q heat radiation incident on target (kW/m^2)
x distance between source and target (m)

τ atmospheric transmissivity

Section 16.19.14
As Section 16.18.6 plus:

b modified lift-off distance
D_j jet diameter (m)
D_s effective source diameter (m)
L flame length (m)

ρ_a density of air (kg/m^3)
ρ_j initial density at jet (kg/m^3)
ρ_v density of vapour (kg/m^3)

Section 16.19.16
F view factor
h height of jet above ground, including any lift-off
L visible length of flame
r_f radius of flame at height z
x distance between axis of jet and target
z height of flame differential element

α half-angle of flame
ψ angular position of flame differential element

Equations 16.19.31 and 16.19.32:
As Section 16.18.6 plus

D_e diameter of cylinder equivalent to flame
L length of cylinder equivalent to flame
L_{BV} height of centre of flame tip above level of jet exit
α_B angle between vertical and line joining jet exit and centre of flame tip
θ angle between vertical and flame axis

Section 16.19.18
A area of ventilation opening (m^2)
H height of ventilation opening (m)

Section 16.20

Section 16.20.1
A wetted surface area
k constant
n index
Q heat absorbed

Equations 16.20.2–16.20.8:
A wetted surface area (ft^2)
q heat absorbed per unit area (BTU/ft^2 h)
Q heat absorbed (BTU/h)

Section 16.20.4
c specific heat of wall metal
d thickness of wall metal
F parameter (see text)
Q heat absorbed per unit area
t time
T_A asymptotic value of T_1
T_o absolute initial wall temperature
T_1 absolute wall temperature at time t

ϵ emissivity of external surface of wall
ρ density of wall metal
σ Stefan–Boltzmann constant

Equations 16.20.12 and 16.20.13:
A parameter defined by Equation 16.20.13
K ratio of outside to inside diameter of wall
P_b burst pressure
T wall temperature (°C)
σ_u ultimate tensile strength of wall metal
σ_y yield strength of wall metal

Section 16.21

Section 16.21.3
I thermal radiation intensity (cal/cm^2 s)
k thermal conductivity of wood (cal/cm^2 s (°C/cm))
t_i ignition time (s)

α thermal diffusivity (cm^2/s)
ρ density of wood (g/cm^2)

Equations 16.21.1–16.21.4:
A parameter defined by Equation 16.21.2 (cal^2/cm^4 (°C)^2)
B parameter defined by Equation 16.21.4 (cal^2/cm^4 (°C)^2
I_p minimum thermal radiation intensity for piloted ignition (cal/cm^2 s)
I_s minimum thermal radiation intensity for spontaneous ignition (cal/cm^2 s)
s specific heat of wood (cal/g °C)

Equations 16.21.5–16.21.18:
c specific heat of wood (cal/g °C)
h heat transfer coefficient for convection (cal/cm^2 s °C)
I_o minimum thermal radiation intensity (cal/cm^2 s)
L linear dimension (cm)
t time (s)
T_o absolute initial temperature (K)
T_s absolute surface temperature for ignition (K)
T_∞ absolute surface temperature for ignition at infinite time (K)
β cooling modulus
γ energy modulus
θ_s absolute surface temperature difference for ignition (°C)
θ_∞ absolute surface temperature difference for ignition at infinite time (°C)

Equations 16.21.19 and 16.21.20:
k_1 constant
L thickness of slab (cm)
n_1–n_3 indices

Section 16.21.4
c specific heat of material
ΔH enthalpy change per unit mass in raising material to its firepoint
k thermal conductivity of material
L 'heating length'
$\dot{q}$ rate of heat transfer across surface
V rate of flame spread

α thermal diffusivity of material
ρ density of material
τ thickness
τ_{cr} critical thickness

Section 16.22

Section 16.22.5
c specific heat of skin
k thermal conductivity of skin
Q net heat absorbed
T_o initial temperature of skin
T_s surface temperature of skin

ρ density of skin

Section 16.22.6
Equation 16.22.2:
I thermal radiation intensity (W/m^2)
n index
t time (s)

Equations 16.22.3 and 16.22.4:
D thermal dose (kJ/m^2)
I thermal radiation intensity (kW/m^2)
L thermal load ((s kW/m^2)$^{\frac{4}{3}}$)
L' thermal load ([s (W/m^2)$^{\frac{4}{3}}$]/10^4)
t exposure time (s)

Equation 16.22.5:
I thermal radiation intensity (W/m^2)
L' thermal load ([s (W/m^2)$^{\frac{4}{3}}$]/10^4)
t exposure time (s)

Section 16.22.13
Equation 16.22.6:
I thermal radiation intensity (W/m^2)
n index
t time (s)

Equation 16.22.7:
a absorptivity of fabric
C specific heat of fabric (J/g °C)
S density of fabric (g/cm^2)
t_p time to piloted ignition (s)
T_o initial temperature of fabric (°C)
T_p piloted ignition temperature (°C)
W incident heat radiation (W/cm^2)

Equation 16.22.8:
D_s clothing ignition load (s(kW/m^2)^2)
I thermal radiation intensity (kW/m^2)
t time (s)

Sections 16.22.15 and 16.22.17
I thermal radiation intensity (W/m^2)
t time of exposure (s)
Y probit

Section 16.22.18
L' thermal load ([s (W/m^2)$^{\frac{4}{3}}$]/10^4)
P_m mortality
P_{ma} average mortality
Y probit

δ burn depth (m)
δ_a burn depth corresponding to average mortality (mm)

Subscripts:
a average
l upper
u lower
1 first coefficient
2 second coefficient

Section 16.26
D mass median drop size (mm)
k_1 constant
n_1, n_2 indices
R rate of water application (l/m^2 s)
R_c critical rate of water application (l/min)
t time to extinguish fire (s)
ΔT difference between water temperature and liquid fire point (°C)

Section 16.27
A surface area of droplet (m^2)
B mass transfer number
c absorption coefficient
C_d drag coefficient
D droplet diameter (m)
g acceleration due to gravity (m/s^2)
G liquid mass flux (kg/m^2 s)
h_d surface enthalpy of droplet (J/kg)
h_s free stream enthalpy (J/kg)
L latent heat of evaporation of droplet (J/kg)
m_d mass of droplet (kg)
M_r rate of evaporation loss due to thermal radiation (kg/s)
Q heat flux droplets (W/m^2) (Equation 16.27.8); heat flux between water and surface (W/m^2) (Equation 16.27.9)
t time (s)
δt time of exposure of droplet (s)
U gas velocity (m/s)
v droplet velocity (m/s)

ν gas kinematic viscosity (m^2/s)
ρ_g gas density (kg/m^3)

Section 16.36
t time (min)
T temperature (°C)

Section 16.36.4
A_T total surface area of walls and ceilings, excluding ventilation openings (m^2)
A_W area of ventilation openings, including doors and windows (m^2)
k_f constant
M_f total mass of combustible material (kg of wood equivalent)
$\dot{m}$ mass burning rate (kg/min)
t_f effective fire resistance time (min)

Section 16.36.11
Equations 16.36.3–16.36.4:
A_W area of ventilation opening (m^2)
H height of ventilation opening (m)
ΔH_c heat of combustion (kJ/kg)
k_v constant (kg/m$^{\frac{3}{2}}$ s)
$\dot{m}$ mass burning rate (kg/s)
$\dot{q}$ heat release rate (kW)

Equations 16.36.5–16.36.8:
A_T total area of enclosure, excluding ventilation openings (m^2)
A_W area of ventilation openings (m^2)
h height of opening (m)
L mass of fuel (kg)
$\dot{q}_{fo}$ heat release rate at flashover (kW)
T_o ambient temperature (°C)
T_u upper limit air temperature (°C)
η ventilation parameter (m$^{-\frac{1}{2}}$)
τ fire load parameter (kg/m^2)

Section 16.36.12
A_f surface area of fuel (m^2)
I thermal radiation intensity (kW/m^2)

L_v	heat of gasification of volatiles (kJ/kg)
$\dot{m}$	mass burning rate (kg/s)
T^*	constant
T_o	absolute ambient temperature (K)
T_u	absolute upper gas temperature (K)
θ_1–θ_5	modification factors (see text)

Section 16.36.13

B	width of window (m)
H	height of window (m)
$\dot{m}$	mass burning rate (kg/s)
n	shape factor defined by Equation 16.36.13
x	horizontal reach of flame (m)
z	height of flame above top of window (m)

Section 16.39

L	length of flame (m)
$\dot{m}$	mass release flow (kg/s)
M	mass of LPG (te)
r	distance to specified lethality (m)
t	exposure time (s)
t_d	duration time (s)
W	half-width of flame at flame tip (m)

Subscripts:

1	1% lethality
50	50% lethality

17 Explosion

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The second of the major hazards is explosion. Explosion in the process industries causes fewer serious accidents than fire but more than toxic release. When it does occur, however, it often inflicts greater loss of life and damage than fire. Explosion is usually regarded as having a disaster potential greater than that of fire but less than that of toxic release.

The *First Report* of the Advisory Committee on Major Hazards (ACMH) (Harvey, 1976) states

> In the case of flammable materials, the greatest threat arises from the sudden massive escape of those volatile liquids, or gases, which could produce a large cloud of flammable, possibly explosive, vapour. If the cloud were ignited, the effects of combustion would depend on many factors including wind speeds and the extent to which the cloud is diluted with air. The worst consequence could be large numbers of casualties and wholesale damage on site and beyond its boundaries. Nevertheless where combustion has taken place it has generally been on or in the immediate vicinity of the site. An important feature of this threat is the small time interval between the initial escape and the fire or explosion, which could be less than a minute.

The Flixborough disaster was primarily due to a vapour cloud explosion. It was this explosion which caused most of the casualties.

There is a considerable literature on explosions. Much of the information relates to chemical or nuclear explosions and to military applications. Reference can be made here only to a few selected texts. These are *Explosions, Their Anatomy and Destructiveness* (C.S. Robinson, 1944), *Explosion and Combustion Processes in Gases* (Jost, 1946), *Supersonic Flow and Shock Waves* (Courant and Friedrichs, 1948), *The Science of High Explosives* (M.A. Cook, 1958), *Combustion, Flames and Explosions of Gases* (B. Lewis and von Elbe, 1961, 1987), *The Effects of Nuclear Weapons* (Glasstone, 1962; Glasstone and Dolan, 1980), *Explosive Shocks in Air* (Kinney, 1962; Kinney and Graham, 1985), *Explosions in Air* (W.E. Baker, 1973) and *Explosion Hazards and Evaluation* (W.E. Baker *et al.*, 1983).

Selected references on explosion are given in Table 17.1 and on detonation in Table 17.2

Table 17.1 *Selected references on explosion (see also Tables 17.2, 17.29, 17.36 and 17.61)*

Explosion, deflagration, detonation
D.J. Lewis (n.d.); Ministry of Defence, ESTC (n.d.); von Schwartz (1904–); Jouguet (1905, 1917); Hopkinson (1915); Chapman (1921); Kratz and Rosencranz (1922); F.W. Stevens (1928); Coward and Hersey (1935 BM RI 3274); Milne-Thompson (1938–, 1947–); C.S. Robinson (1944); Kirkwood and Brinkley (1945); Jost (1946); G.I. Taylor (1946); Brinkley and Kirkwood (1947, 1949, 1961); Smart (1947); Courant and Friederichs (1948); Doering and Burkhardt (1949); Bowden and Yoffe (1952); Zabetakis and Jones (1955); Burgoyne (1956); K.N. Palmer (1956); Glasstone (1957, 1962, 1964); Randall *et al.* (1957); Emmons (1958); Ghormley (1958); Brinkley and Lewis (1959); Penner and Mullins (1959); Pipkin (1959); Rinehart (1959); Anon. (1960a); M.W. Evans and Ablow (1961); B. Lewis and von Elbe (1961, 1987); J.K. Wright (1961); J.N. Bradley (1962); Kinney (1962, 1968); Ginsburgh and Bulkley (1963, 1964); Yakovlev (1963); Jacobs (1964); Jacobs, Blunk and Scheineman (1964); Markstein (1964); Muzzall (1964); Oswatitsch (1965); Zabetakis (1965); Fordham (1966); Kogarko, Adushkin and Lyamin (1966); Laderman (1966); Soloukhin (1966, 1969); Urtiew and Oppenheim (1965, 1966, 1967, 1968); Craven and Greig (1967); P. Gray and Lee (1967a,b); Liepman and Roshko (1967); Burgess *et al.* (1968 BM RI 7196); E. Cohen (1968); D.L. Jones (1968, 1970); Lutzsky and Lehto (1968); Munday, Ubbelohde and Wood (1968); H.S. Robinson (1968); Strehlow (1968a,b); van Dolah (1969b); Nagy, Conn and Verakis (1969 BM RI 7279); van Dolah and Burgess (1968); Ubbelohde and Munday (1969); Pawel *et al.* (1970); Rasbash (1969c, 1970a, 1976a,b); Furno *et al.* (1971); Gruschka (1971); Klaassen (1971); Munday (1971b); Nagy *et al.* (1971 BM RI 7507); Panton (1971); Cubbage and Marshall (1972, 1973, 1974); Alexander and Taylor (1973a,b); W.E. Baker (1973); W.E. Baker, Westine and Dodge (1973); Grein (1973); Guill (1973); Hatfield (1973); Sadee (1973a,b); Bartknecht (1974a, 1980, 1981a); Hess, Hoffmann and Stoeckel (1974); W.G. High (1974, 1976); NFPA (1974/12); Perlee, Fuller and Saul (1974 BM RI 7839); Raj and Kalelkar (1974); Sivashinsky (1974); W.E. Baker *et al.* (1975); Eisenberg, Lynch and Breeding (1975); Groothuizen and Pasman (1975); Kanury (1975); Kassoy (1975); Swisdak (1975); MITI (1976); Strehlow and Baker (1975, 1976); AIChE (1976/69); J.W. Watts (1976); Fiumara (1977); Kletz (1977c, 1977–78); Leiber (1977); V.C. Marshall (1977a,b,d, 1987, 1990b); Stull (1977); W.E. Baker *et al.* (1978); HSE (1978b, 1981a); R. King and Magid (1979); Pohto (1979); Bartknecht *et al.* (1980); Bodurtha (1980); Yallop (1980); Croft (1980/81); J.G. Marshall and Rutledge (1982); Mecklenburgh (1982, 1985); Pantony and Smith (1982); Ramsay, Sylvester-Evans and English (1982); Solberg (1982a,b); Zeeuwen (1982); W.E. Baker *et al.* (1983); Anon. (1984qq); J.R. Bowen *et al.* (1984a,b); J.F. Clarke and Kassoy (1984); Kinney and Graham (1985); Cruice (1986); Fordham Cooper (1986); Pasman and Wagner (1986); C.K. Chan and Greig (1989); FPA (1989 CFSD FS 6011); ILO (1989); Teodorczyk, Lee and Knystautas (1989); Lazari, Burley and Al-Hassani (1991); Makhviladze and Rogatykh (1991); Pineau *et al.* (1991); D.C. Bull (1992); CPD (1992a,b); Opschoor, van Loo and Pasman (1992); Lefebvre *et al.* (1993)

Explosion energy (*see also* Tables 17.29 and 17.36)
Girdhar and Aurora (1977); Hardesty and Kennedy (1977); Kinney and Graham (1985); Crowl (1991, 1992a); CCPS (1994/15)
Gas-filled vessels: Brode (1955, 1957, 1959); Kinney (1962); Kiwan (1970a,b, 1971); W.E. Baker (1973); Strehlow and Ricker (1976); Pohto (1979); Polentz (1980); Aslanov and Golinsky (1989); Crowl (1992a); CCPS (1994/15)

Explosion scaling
C.J.M. van Wingerden (1989b); Catlin and Johnson (1992)

Flame acceleration, deflagration to detonation transition (DDT) (see also Table 17.29)

Markstein (1957); Thibault *et al.* (1982); Lee, Knystautas and Freeman (1984); Stock, Schildknecth and Geier (1984); S.B. Murray and Lee (1984); Peraldi, Knystautas and Lee (1986); Nettleton (1987); Lindstedt and Michels (1989); Moen *et al.* (1989); C.K. Chan, Lau and Radford (1991)
Pipes, tubes: M.W. Evans *et al.* (1949); Holzapfel and Schon (1965); Craven and Greig (1967); Leyer and Manson (1971); Moen, Murray *et al.* (1982); Rinnan (1982); J.F. Clarke and Kassoy (1984); Picone *et al.* (1984); Taki and Fujiwara (1984); Lee, Knystautas and Chan (1985); Dunn-Rankin, Barr and Sawyer (1986); Ungüt and Shuff (1989); Dupré *et al.* (1991); Phylaktou, Andrews and Herath (1990); C.K. Chan, Lau and Radford (1991); Phylaktou and Andrews (1991a,b); Phylaktou, Foley and Andrews (1993); CCPS (1994/15)
Enclosures, modules: Urtiew (1981); Moen (1982a); Hjertager *et al.* (1984); J.R. Harris and Wickens (1989); Hjertager (1991); K. van Wingerden, Visser and Pasman (1991)
Vapour clouds: Urtiew (1982a); H.G. Wagner (1982); Nettleton (1987); CCPS (1994/15)

Combustion in pipes
Mason and Wheeler (1917, 1920a–c); Chapman and Wheeler (1926, 1927); Fenning (1926); de C.O.C. Ellis and Wheeler (1925, 1928a,b); Kirby and Wheeler (1931a,b); H. Robinson and Wheeler (1933); D.T. Williams and Bollinger (1949); Guenoche (1964); Gugan (1974b); Dörge, Pangritz and Wagner (1981); Moen, Lee *et al.* (1982); Hjertager (1984); J.H.S. Lee, Knystautas and Chan (1985); Hjertager, Bjorkhaug and Fuhre (1988); Hjertager, Fuhre and Bjorkhaug (1988a)

Combustion in partially confined spaces
Abou-Arab, Erayet and Kamel (1991)
Parallel plates: Moen, Donato, Knystautas and Lee (1980); Moen, Donato, Knystautas, Lee and Wagner (1980); C.J.M. van Wingerden and Zeeuwen (1983); Hjertager (1984); C.J.M. van Wingerden (1984, 1989c)
Channels: Urtiew (1981); C. Chan, Moen and Lee (1983); Elsworth, Eyre and Wayne (1983); Sherman *et al.* (1985); P.H. Taylor (1986)

Spherical and cylindrical explosions (*see also* Tables 17.13 and 17.29)
Cousins and Cotton (1951a–b); Crouch *et al.* (1952); Vance and Krier (1974); Frankel and Sivashinsky (1983)

Explosions in vessels (*see also* Table 17.13)
Creech (1940); G.F.P. Harris and Briscoe (1967); Perlee, Fuller and Saul (1974 BM RI 7839); Sibulkin (1980); S.R. Moore and Weinberg (1981); Grewer and Klais (1987); Rota *et al.* (1987); Phylaktou, Andrews and Herath (1990); Phylaktou and Andrews (1991b, 1993); Checkel and Thomas (1994); Phylaktou, Andrews and Liu (1994)
Spherical geometry, spherical vessels: Flamm and Mache (1917); Mache (1918); Grumer, Cook and Kubala (1959); Spalding (1960); Spalding and Jain (1961); Spalding, Jain and Samain (1961); Raezer (1961); Pliickebaum, Strauss and Edse (1964); G.F.P. Harris (1967); Nagy, Conn and Verakis (1969 BM RI 7279); D. Bradley and Mitcheson (1976); Groff (1982); Kumar, Tamm and Harrison (1983); McCann, Thomas and Edwards (1985); Champion *et al.* (1986); Hjertager, Bjorkhaug and Fuhre (1988); Cant and Bray (1989); A.A. Evans (1989, 1990, 1991, 1992a,b); Tanaka (1989); Canu *et al.* (1990)
Cylindrical geometry, cylindrical vessels: Jain and Ebenzer (1966); Vance and Krier (1974); Starke and Roth (1986, 1989); Andrews, Herath and Phylaktou (1990)

Pressure piling
Beyling (1906); Grice and Wheeler (1929); Coward and Wheeler (1934); Gleim and March (1952 BM RI 4904); T.A.J. Brown (1959); K.C. Brown and Curzon (1963); Heinrich (1975); J. Singh (1977, 1984, 1994a); Bartknecht (1981a); Boyd *et al.* (1981); Fitt (1981a,b); Zeeuwen (1981); Phylaktou and Andrews (1993)

Other enhanced pressure effects
Kordylewski and Wach (1986, 1988)

Explosions in enclosures, modules
Rasbash (1976b,d); DnV (1979 79–0483); Hirano (1984); Hjertager *et al.* (1984); Hjertager (1986, 1991, 1993); Hjertger, Bjorkhaug and Fuhre (1988); Catlin (1991); Takahashi *et al.* (1991); Catlin and Johnson (1992); Hjertager, Solberg and Nymoen (1992); Phylaktou *et al.* (1992); Catlin, Manos and Tite (1993); Samuels (1993); Phylaktou, Andrews and Liu (1994); K. van Wingerden, Pedersen and Wilkins (1994)

Explosions in buildings
Astbury *et al.* (1970); Cubbage and Moppett (1970); FRS (1971 Fire Res. Note 847, 1974 Fire Res. Note 984, 985); Fry (1971); Astbury, West and Hodgkinson (1972, 1973); Astbury and Vaughan (1972); W.B. Howard (1972); BRE (1973 CP 11/73, 1974 BR9, CP 45/74, 1976 CP 24/76); Bartknecht (1981a); Buckland (1980); Zalosh (1980a); R.J. Harris (1983); Cleaver, Marshall and Linden (1994)
Ronan Point: H. Griffiths, Pugsley and Saunders (1968)

Bursting vessels
Boyer *et al.* (1958); M.P. Friedman (1961); Garrison (1975); Leslie and Birk (1991); Gelfand *et al.* (1992)

Vented explosions
Hjertager (1982a,b, 1986, 1991); P.H. Taylor (1986); Hjertager, Fuhre and Bjorkhaug (1988a,b); Bakke *et al.* (1989); van den Berg, van Wingerden and Verhagen (1989); P.H. Taylor and Bimson (1989); C.J.M. van Wingerden (1989c); Tamanini and Chaffee (1992).
CLICHE: Catlin (1990)
FLACS: Hjertager (1982a); Bakke, Bjerketvedt and Bjorkhaug (1990)

Explosive loads
ACDS (1991); Gilbert, Lees and Scilly (1994a–c)

Particular types of explosion
Adsorbers: Anon. (1986 LPB 69, p.25); CCPS (1993/13)
Air plants: Rotzler *et al.* (1960); Matthews (1961); G.T. Wright (1961); Lang (1962, 1965); Rendos (1963); Boyne (1966)
Air systems, oil films: Mallow (1964a,b); Thoenes (1964); Sichel, Rao and Nicholls (1971); Burgoyne and Craven (1973); Fowle (1973)

Ammonium nitrate: Commentz *et al.* (1921); Kintz, Jones and Carpenter (1948 BM RI 4245); National Board of Fire Underwriters (1948); Hainer (1955); Sykes, Johnson and Hainer (1963); Sykes *et al.* (1963); van Dolah *et al.* (1966 BM RI 6747, RI 6773); HSE (1978b); Heemskerk and Schuurman (1989); ACDS (1991)
Asphalt, bitumen tanks: Anon. (1986 LPB 71, p. 71); Trumbore, Williamson and Wolfsberger (1991); Davie, Nolan and Hoban (1993, 1994); Davie, Nolan and Tucker (1993)
Boilers: Ostroot (1976b); Hewison (1983); G.D. Davis (1987); Bond (1990 LPB 93)
Centrifuges: Butterwick (1976); Funke (1976); Lindley (1987)
Chlorine systems: Eichelberger, Smura and Bergenn (1961); Johnsen and Yahnke (1962, 1973); Dokter (1985a,b); Tabata, Kodama and Kotoyori (1987); Baillou *et al.* (1992)
Compressors: Gibbs (1960); Perlee and Zabetakis (1963 BM RI 8187); Walton (1963); W.L. Ball (1964); Schmitt (1964); Strelzoff (1964); Thoenes (1964); J.A. Rogers (1965); Armistead (1973); Burgoyne and Craven (1973); Fowle (1973); Prentice, Smith and Virtue (1974); HSE (1978b); Anon. (1979 LPB 26, p. 51); Kolodner (1980)
Cooling systems: Mansfield (1990 LPB 94)
Crankcase: Burgoyne, Newitt and Thomas (1954); Burgoyne and Newitt (1955); Mansfield (1956); Freestone, Roberts and Thomas (1965); Rushbrook (1979)
Diesel engines: Anon. (1970d)
Distillation systems: Carrara (1973); *Fire Journal* Staff (1973a); Freeman and McReady (1971); Jarvis (1971); Keister, Pesetsky and Clark (1971); Griffith and Keister (1973); Kotoyori *et al.* (1976); Kroger (1979)
Driers: K.N. Palmer (1973a); Reay (1977); Bartknecht (1981a); Abbott (1990); Schoofs (1992); Anon. (1994 LPB 119, p. 5)
Drums and small tanks: HSE (1970 Bklt 32); Pinsky, Vickery and Freeman (1990); Anon. (LPB 103, p. 31)
Electrical: Benjaminsen and van Wiechen (1968); Fordham Cooper (1986); Bartels (1990)
Ethylene: Martinot (1984); Vanderwater (1989)
Ethylene oxide systems: Troyan and Levine (1968); Ogawa, Miyake and Matsuo (1992)
Extruders: Anon. (1986 LPB 71, p. 31); Carter (1987 LPB 73); Anon. (1989 LPB 87, p. 3)
Flare systems: Bluhm (1964b); Kilby (1968)
Furnaces: P. Peterson (1967); Kletz (1972c); Ostroot (1972, 1976b); Durrant and Lansing (1976); Anon. (1992 LPB 108, p. 17)
Gas distribution system (public supply): DoEn (1977b); Buckland (1980); R.J. Harris (1983)
Heat exchangers: Zabetakis (1960 BM RI 5645); Bohlken (1961); Mesloh (1964); Lang (1965); Anon. (1987 LPB 74, p. 15); Anon. (1987 LPB 75, p. 22); Cullen (1990)
Hydraulic accumulators: Pratt (1986)
Hydrogen: Kolodner (1980); Anon. (1984x); Nordmo and Emblem (1989); Tamanini *et al.* (1989)
Incinerators: Anon. (1988 LPB 81, p. 17); Anon. (1990 LPB 92, p. 29)
Liquefied natural gas: Anon. (1972f); HSE (1978b); ACDS (1991)
Liquefied petroleum gas: HSE (1978b); Rasbash (1979/80); ACDS (1991)
Low temperature fluids: Burgoyne (1965b)
Lubricants: Anon. (1960c); Burgoyne and Craven (1973); Hasegawa (1992)
Mist and spray: Haber and Wolff (1923); Burgoyne and Richardson (1949b); Burgoyne (1957); Eichhorn (1964); J. R. Bowen *et al.* (1971); Vincent and Howard (1976); Vincent *et al.* (1976a,b); Gubin and Sichel (1977); Nettleton (1977b, 1987); Bar-or, Sichel and Nicholls (1981, 1982); Dabora (1982); Sichel (1982a,b); Sichel and Palaniswamy (1985); Bothe, Brandes and Redeker (1986)
Molten metal: Genco and Lemmon (1970)
Molten metal–water: C.F. Epstein (1961); Lipsett (1966); Brauer, Green and Mesler (1968); Flory, Paoli and Mesler (1969); Konway, Mead and Page (1975); HSE (1977/8); Vaughan (1980 SRD R177)
Nitrogen systems: Conklin (1961); Sanders and Nordop (1963); J.A. Rogers (1965); Anon. (1979 LPB 29, p. 151)
Piping: J.B. Smith (1949); Ringer (1985); Anon. (1989 LPB 88, p. 13)
Pollution control equipment: K.N. Palmer (1973a); Bodurtha (1976)
Pumps: Anon. (1987 LPB 74, p. 23)
Rail tank cars: Vanderwater (1989)
Ships: Burgoyne (1965a); Page and Gardner (1971); V.J. Clancey (1981); Blything and Edmonson (1984 SRD R292); ACDS (1991)
Spray driers: Masters (1972–, 1979); N. Gibson and Schofield (1977); Bartknecht (1981a)
Storage tank 'pops': Anon. (1988 LPB 82, p. 12); Kletz (1988 LPB 83)
Superheat: D.L. Katz (1972); R. King (1975a–c, 1976a,b, 1977); R.W. King (1976); Porteous and Blander (1975); Reid (1976)
Tanks, including storage tanks: Kletz (1971); Leiber (1980); HSE (1981 SHW 2125); McDaniel (1986); Anon. (1987 LPB 73, p. 9)
Vaporizers: Wright (1961)
Vent flashback: Burgoyne (1986a); W.B. Howard (1992a,b)

'Flameless' or 'physical' explosions, LNG/water explosions, rapid phase transition explosions, steam explosions

Witte, Cox and Bouvier (1970); D.L. Katz and Sliepcevich (1971); Enger and Hartman (1972a); D.L. Katz (1972); W. Nelson (1973a,b); Yang (1973); Opschoor (1974); Porteous and Blander (1975); Porteous and Reid (1976); Reid (1976, 1978); AGA (1977/26); Dincer, Drake and Reid (1977); Briscoe and Vaughan (1978 SRD R131); Witte and Cox (1978); Hogan (1982); Fauske and Henry (1983); McRae (1983); Ogiso, Fujita and Uehara (1986); Ogiso, Takagi and Katagawa (1986); D.C. Bull and Strachan (1992); Fletcher and Theofanous (1994)

Table 17.2 *Selected references on detonation*

B. Lewis and Friauf (1930); C. Campbell, Littler and Whitworth (1932); Payman and Titman (1935); Zeldovich (1940); von Neumann (1942); Döring (1943); Brinkley and Kirkwood (1947, 1949); Ubbelohde (1949, 1953); Berets, Greene and Kistiakowsky (1950); G.I. Taylor (1950); Fay (1952, 1962); R. Friedman (1953); Hirschfelder, Curtiss and Campbell (1953); Manson and

Ferri (1953); Oppenheim (1953, 1969); Chester (1954); Gerstein, Carlson and Hill (1954); Weir and Morrison (1954); Zeldovich, Kogarko and Semenov (1956); Chisnell (1957); Adams and Pack (1959); Brinkley and Lewis (1959); M.A. Cook, Pack and Gey (1959); D.H. Edwards, Williams and Breeze (1959); Eisen, Gross and Rivlin (1960); Zeldovitch and Kompaneets (1960); Brinkley and Kirkwood (1961); M.W. Evans and Ablow (1961); Gvozdeva (1961); Randall and Ginsburgh (1961); Sommers (1961); Wehner and Phillips (1962); Boddington (1963); Freiwald and Koch (1963); Litchfield, Hay and Forshey (1963); Oppenheim and Rosciszewski (1963); Spalding (1963b); H.G. Wagner (1963); Mitrovanov and Soloukhin (1964); Monger *et al.* (1964); Dabora, Nicholls and Morrison (1965); J.J. Lee, Lee and Shanfield (1965); Strehlow and Fernandes (1965); Urtiew and Oppenheim (1965, 1966, 1967, 1968); Litchfield and Hay (1966 BM RI 6840, 1967 BM RI 7061); de Malherb *et al.* (1966); Solouokhin (1966, 1969); Strehlow, Crooker and Cusey (1967); Strehlow *et al.* (1967); Skinner *et al.* (1968); Strehlow (1968, 1971); Zeldovich and Raiza (1968); Brinkley and Seely (1969); E.L. Lee and Hornig (1969); Lundstrom and Oppenheim (1969); Strehlow and Biller (1969); Strehlow and Engle (1969); Trezek and Balcerzak (1969); Ubbelohde and Munday (1969); Zajac and Oppenheim (1969); J.W. Meyer, Urtiew and Oppenheim (1970); Pawel *et al.* (1970); Nagaishi, Yoneda and Hikita (1971); Panton (1971); Vasilev, Gavrilenko and Topchian (1972); Carlson (1973); Whitham (1974); Fry and Nicholls (1975); J.H. Lee, Knystautas and Guirao (1975, 1982); Sloan and Nettleton (1975, 1978); Takai, Yoneda and Hikita (1975); D.C. Bull *et al.* (1976); Chiu and Lee (1976); Knystautas and Lee (1976); J.H. Lee and Ramamurtha (1976); Matsui and Lee (1976, 1979); J.H.S. Lee (1977, 1980); J.H. Lee and Matsui (1977); Benedick (1979); D.C. Bull, Elsworth and Hooper (1979a,b); D.H. Edwards, Thomas and Nettleton (1979, 1983); Fickett and Davis (1979); Knystautas *et al.* (1979); Mader (1979); van der Molen and Nicholls (1979); Nicholls *et al.* (1979); R. Atkinson, Bull and Shuff (1980); Moen *et al.* (1980); Sibulkin (1980); Bowers *et al.* (1981); Edwards *et al.* (1981); Eidelman and Burcat (1981); Moen *et al.* (1981); Oran *et al.* (1981); Urtiew and Tarver (1981); Wolanski *et al.* (1981); Abouseif and Toong (1982a,b, 1986); D.C. Bull *et al.* (1982); Burcat and Hasson (1982); Dabora (1982); Damamme (1982); Eidelman (1982); Guirao *et al.* (1982); Knystautas, Lee and Guirao (1982); Logan and Bdzil (1982); Moen, Lee *et al.* (1982); Moen, Murray *et al.* (1982); Oran *et al.* (1982); Tarver (1982); Westbrook (1982a,b); Westbrook and Urtiew (1982); J.R. Bowers *et al.* (1983); Elsworth and Eyre (1984); Elsworth, Shuff and Ungut (1984); Kailasanath and Oran (1984); Ohyagi, Yoshihashi and Harigaya (1984); Vandermeiren and van Tiggelen (1984); Westbrook, Pitz and Urtiew (1984); Kailasanath *et al.* (1985); Kuznetsov and Kopotev (1985); Moen, Bjerketvedt *et al.* (1985); Moen, Ward *et al.* (1985); Presles *et al.* (1985); Moen, Sulmistras *et al.* (1986); Weinberg (1986); Huang Zhong-Wei and Xu Bin (1987); Nettleton (1987); Linstedt and Michels (1988); Zerilli *et al.* (1988); Bauer *et al.* (1989); Knystautas *et al.* (1989); Moen *et al.* (1989); G.O. Thomas, Sutton and Edwards (1991); Bourlioux and Majda (1992); He and Clavin (1992); Lefebvre *et al.* (1993); Moen (1993)

17.1 Explosion

17.1.1 The explosion process

An explosion is a sudden and violent release of energy. The violence of the explosion depends on the rate at which energy is released. The energy stored in a car tyre, for example, is capable of causing an explosive burst, but it can be dissipated by gradual release.

There are several kinds of energy which may be released in an explosion. Three basic types are (1) physical energy, (2) chemical energy and (3) nuclear energy.

Physical energy may take such forms as pressure energy in gases, strain energy in metals or electrical energy. Examples of the violent release of physical energy are the explosion of a vessel due to high gas pressure and the sudden rupture of a vessel due to brittle fracture. Another important physical form is thermal energy. This is generally important in creating the conditions for an explosion rather than as a source of energy for the explosion itself. In particular, superheat in a liquid under pressure causes flashing off of the liquid if it is let down to atmospheric pressure.

Chemical energy derives from a chemical reaction. Examples of the violent release of chemical energy are explosion of a vessel due to combustion of flammable gas, and explosion of a reactor caused by decomposition of reaction products in a runaway chemical reaction.

Chemical explosions are either (1) uniform explosions or (2) propagating explosions. An explosion in a vessel tends to be a uniform explosion, while an explosion in a long pipe gives a propagating explosion.

Nuclear energy is not considered here. In the present context, it is chemical explosions, and in particular explosions resulting from combustion of flammable gas, which are of prime interest.

17.1.2 Deflagration and detonation

Explosions from combustion of flammable gas are of two kinds: (1) deflagration and (2) detonation.

In a deflagration the flammable mixture burns relatively slowly. For hydrocarbon–air mixtures the deflagration velocity is typically of the order of 1 m/s.

A detonation is quite different. In a detonation the flame front travels as a shock wave followed closely by a combustion wave which releases the energy to sustain the shock wave. At steady state the detonation front reaches a velocity equal to the velocity of sound in the hot products of combustion and thus much greater than the velocity of sound in the unburnt mixture. For hydrocarbon–air mixtures the detonation velocity is typically of the order of 2000–3000 m/s. For comparison the velocity of sound in air at 0°C is 330 m/s.

A detonation generates greater pressures and is more destructive than a deflagration. Whereas the peak pressure caused by the deflagration of a hydrocarbon–air mixture in a closed vessel is of the order of 8 bar, a detonation may give a peak pressure of the order to 20 bar.

A deflagration may turn into a detonation, particularly when travelling down a long pipe. Where a transition from deflagration to detonation is occurring, the deflagration velocity naturally exceeds that quoted above.

Deflagration and detonation are discussed further in Sections 17.2, 17.5 and 17.6.

17.1.3 Process industries explosions: explosions vs fires

Some data on 83 large loss fires/explosions over a 5 year period have been given by W.H. Doyle (1969), and were reproduced in Table 2.14. These data have been expressed by Kletz (1977k) in terms of the proportion of fires and of explosions of different types:

	Proportion (%)
Explosions inside equipment because air got in	11
Explosions inside equipment because of runaway reactions or explosive decomposition	23
Explosions outside equipment but inside buildings	24
Explosions in the open	3
Vessels bursting (due to corrosion, overheating or overpressure)	7
Fires	32
Total	100

17.1.4 Process industries explosions: classification of explosions

Explosions in the process industries include the following types:

(1) physical explosions –
  (a) mechanical failure of pressure system (within design envelope),
  (b) overpressure of pressure system,
  (c) underpressure of pressure system,
  (d) overtemperature of pressure system,
  (e) undertemperature of pressure system;
(2) condensed phase explosions –
  (a) high explosives,
  (b) ammonium nitrate,
  (c) organic peroxides,
  (d) sodium chlorate;
(3) vapour cloud explosions (VCEs);
(4) boiling liquid expanding vapour explosions (BLEVEs);
(5) confined explosions with reaction –
  (a) explosion involving vapour combustion,
  (b) reactor explosions,
  (c) other explosions involving liquid phase reactions;
(6) vapour escapes into, and explosions in, buildings (VEEBs);
(7) dust explosions.

17.2 Detonation

A particularly severe form of explosion occurs when an explosive substance detonates. Detonation can occur in liquid and solid explosives, in explosive gas mixtures inside plant and in vapour clouds. These aspects of detonation are considered in Sections 17.3, 17.6 and 17.28.

Accounts of detonation, and of shock waves, are given in *Supersonic Flow and Shock Waves* (Courant and Friederichs, 1948), *Theory of Detonation* (Zeldovich and Kompaneets, 1960), *Shock Waves in Chemistry and Physics* (J.N. Bradley, 1962), *Gas Dynamics of Combustion* (Shchelkin and Troshin, 1965), *Shock Waves and Detonations in Gases* (Soloukhin, 1966), *Fundamentals of Combustion* (Strehlow, 1968a), *Detonation* (Fickett and Davis, 1979), *Unconfined Vapour Cloud Explosions* (Gugan, 1979), *The Effects of Nuclear Weapons* (Glasstone and Dolan, 1980), *Explosive Shocks in Air* (Kinney and Graham, 1985), *Principles of Combustion* (Kuo, 1986), *Combustion, Flames and Explosions of Gases* (B. Lewis and von Elbe, 1987) and *Gaseous Detonations* (Nettleton, 1987).

The origins of work on detonations are to be found in explosion disasters, notably in coal mines, and in the mathematical theory of shock waves. Studies by Riemann showed that even starting from smooth initial conditions the movement of compressible gases can lead to formation of discontinuities with a sudden rise in pressure and temperature. The thermodynamics of shock waves were investigated by Hugoniot (1887–89). The extension to reactive systems then led to the detonation theory of Chapman (1899) and of Jouguet (1905).

The Chapman–Jouguet equations, however, were consistent with a number of final states. The choice of final state was made by these workers on the basis of a minimum velocity criterion. Their studies provided a working model which in certain features gave good agreement with experiment and held the field for some 40 years.

A further advance came with the concept of the initiation of combustion by a shock wave travelling ahead of the reaction zone, proposed independently by Zeldovich (1940), von Neumann (1942) and Döring (1943). This theory takes into account the finite rate of the chemical reactions.

Later work has shown, however, that the Zeldovitch–von Neumann–Döring (ZND) model is unstable for the case where the reactions are strongly temperature dependent. There still exists, therefore, no comprehensive theory of detonations.

Another aspect of interest here is the transition from deflagration to detonation, to which a particular contribution has been made by Shchelkin (Shchelkin and Troshin, 1965).

Much work on detonation utilizes mixtures of fuel with oxygen rather than air. Hence, care should be exercised in reading the literature to check the oxidant to which a particular statement or correlation is applicable.

Selected references on detonation are given in Table 17.2, and on detonability characteristics in Table 17.3.

17.2.1 Detonation waves

In a detonation, a detonation wave passes through the explosive substance. This detonation wave has certain well defined properties. These are now considered.

The detonation wave may develop by a process of transition. This transition may be illustrated by considering the combustion in a tube of a flammable gas–air mixture which is initially at constant pressure. If ignition occurs and energy is released at one end of the tube, the burnt gases expand. The deflagration front moves at a flame speed which is the sum of the burning velocity and the velocity of the burnt gases. If the flame speed is low enough, the combustion continues at essentially constant pressure, but if the flame speed is sufficiently high for momentum changes to exercise a significant

Table 17.3 *Selected references on detonability characteristics*

Explosibility, flammability (*see* Tables 8.1, 16.3 and 17.62)

Detonation limits and velocity (also cell size, critical tube diameter, critical initation energy)
Hirschfelder, Curtiss and Campbell (1953); Ghormley (1958); Belles (1959); Shchelkin (1959); B. Lewis and von Elbe (1961); Burgess *et al.* (1968 BM RI 7196); Benedick, Kennedy and Morosin (1970); Michels, Munday and Ubbelohde (1970); Benedick, Morosin and Kennedy (1971); Munday (1971b); Carlson (1973); Nolan (1973); Strehlow (1973b); J.W. Watts (1976); Borisov and Loban (1977); J.H. Lee and Matsui (1977); Nettleton (1978a, 1979, 1980a,b, 1987); Moen *et al.* (1981); J.H.S. Lee, Knystautas and Guirao (1982); Bauer, Brochet and Presles (1984); Kailasanath and Oran (1984); Vandermeiren and van Tiggelen (1984); Knystautas *et al.* (1984); Bauer, Presles and Heuze (1986); Michels and Rashidi (1992); Rashidi and Michels (1992)

effect, pressure disturbances are created. In this latter case the flame front accelerates and travels as a combustion wave preceded by a shock wave. Further acceleration of the flame front may cause the deflagration to turn into a detonation. The detonation wave then travels with a velocity greater than that of sound in the unburnt gas.

17.2.2 Unidimensional models

Analysis of the behaviour of shock waves with and without reaction was for many years conducted mainly in terms of models in one dimension. Although the deficiencies of these unidimensional models are now recognized, they have been very successful in describing some important properties of the waves.

17.2.3 Non-reactive shock wave

It is convenient to consider first the unidimensional model of a planar shock wave in a non-reactive medium. Conventionally, the model is given with a co-ordinate system moving with the wavefront. The basic equations are

$$\frac{u_1}{v_1} = \frac{u_2}{v_2} \qquad \text{Conservation of mass} \qquad [17.2.1]$$

$$p_1 + \frac{u_1^2}{v_1} = p_2 + \frac{u_2^2}{v_2} \qquad \text{Conservation of momentum} \qquad [17.2.2]$$

$$h_1 + \frac{1}{2}u_1^2 = h_2 + \frac{1}{2}u_2^2 \qquad \text{Conservation of energy} \qquad [17.2.3]$$

with

$$h = e + pv \qquad [17.2.4]$$

$$pv = RT \qquad [17.2.5]$$

$$v = 1/\rho \qquad [17.2.6]$$

where e is the specific internal energy of the gas, h is its specific enthalpy, p is the pressure, u is the velocity of the gas, v is its specific volume, T is its absolute temperature, ρ is its density, and the subscripts 1 and 2 are the gas entering and leaving the shock wave, respectively.

From Equations 17.2.1–17.2.4

$$h_2 - h_1 = \frac{1}{2}(p_2 - p_1)(v_1 + v_2) \qquad [17.2.7]$$

$$e_2 - e_1 = \frac{1}{2}(p_2 + p_1)(v_1 - v_2) \qquad [17.2.8]$$

Other useful relations are, from Equations 17.2.1, 17.2.2 and 17.2.6,

$$(\rho_1 u_1)^2 = \frac{p_2 - p_1}{v_1 - v_2} \qquad [17.2.9]$$

and from this equation and Equation 17.2.6

$$u_1 = v_1\left(\frac{p_2 - p_1}{v_1 - v_2}\right)^{\frac{1}{2}} \qquad [17.2.10]$$

The internal energy change Δe is

$$\Delta e = e_2 - e_1 \qquad [17.2.11]$$

$$= \bar{c}_v(T_2 - T_1) \qquad [17.2.12]$$

where $\bar{c}_v$ is the mean specific heat at constant volume.

The particle velocity w is

$$w = u_1 - u_2 \qquad [17.2.13]$$

and it may be written, utilizing Equations 17.2.1 and 17.2.10, as

$$w = (v_1 - v_2)\left(\frac{p_2 - p_1}{v_1 - v_2}\right)^{\frac{1}{2}} \qquad [17.2.14]$$

Another parameter of interest is the 'impulse' i, which is a measure of the pressure exerted by the shock wave on an obstacle over and above the pressure difference $(p_2 - p_1)$. The total pressure exerted is $\rho_2 w^2$. Then, substituting for this term using Equations 17.2.6 and 17.2.14 and subtracting the term $(p_2 - p_1)$, the net pressure i is

$$i = \frac{v_1}{v_2}(p_2 - p_1) \qquad [17.2.15]$$

For the case where the co-ordinates of the system are with respect to a fixed frame of reference, rather than moving with the shock wave, the velocity of the shock wave is

$$D = V_1 + u_1 \qquad [17.2.16]$$

where D is the velocity of the shock wave and V_1 is the velocity of the gas entering the shock wave, both in the fixed frame of reference. But since for the unburned gas $V_1 = 0$,

$$D = u_1 \qquad [17.2.17]$$

The two co-ordinate systems are discussed by Kuo (1986) and B. Lewis and von Elbe (1987).

Table 17.4 *Some shock wave parameters for air (after Becker, 1922)*

$\frac{p_2}{p_1}$	$\frac{v_1}{v_2}$	D (m/s)	w (m/s)	T_2 *shock wave* (K)	T_2 *adiabatic compression* (K)	$\frac{i}{p_1}$
2	1.63	452	175	336	330	1.63
5	2.84	698	452	482	426	11.4
10	3.88	978	725	705	515	34.9
100	7.06	3020	2590	3860	950	699

From Equations 17.2.10 and 17.2.17

$$D = v_1\left(\frac{p_2 - p_1}{v_1 - v_2}\right)^{\frac{1}{2}} \qquad [7.2.18]$$

Values of the shock wave parameters for air calculated by Becker (1922) are shown in Table 17.4.

For the case of detonation, in which a reaction occurs in the shock wave and the energy conservation equation is augmented by a heat input term, as discussed below, D becomes the detonation velocity.

17.2.4 Rankin–Hugoniot curves

Equation 17.2.7 is the Rankin–Hugoniot (R–H) equation. The equation shows the relation between the initial and final states for a given change of enthalpy across the shock front. For an ideal gas with a constant ratio of specific heats γ, Equation 17.2.7 may be reformulated as

$$\frac{\gamma}{\gamma - 1}(p_1 v_1 - p_2 v_2) = \frac{1}{2}(p_2 - p_1)(v_1 + v_2) \qquad [17.2.19]$$

Equation 17.2.19 yields in the p–v plane a curve which is a rectangular hyperbole. Such a curve is known as a R–H curve. Various forms of the curve are shown in Figure 17.1. Figure 17.1(a) shows for comparison an R–H curve and a curve for an isentropic process $pv^{\gamma} = \text{constant}$. Equation 17.2.9 gives a line between a pair of points on the R–H curve which is known as a Rayleigh line. Figure 17.1(a) also shows such a line.

On the assumption that there is no change in the molecular weight or ratio of specific heats of the gas, Equations 17.2.1–17.2.3, 17.2.5 and 17.2.6 yield

$$\frac{p_2}{p_1} = \frac{2\gamma\,\mathrm{Ma}_s^2 - (\gamma - 1)}{\gamma + 1} \qquad [17.2.20]$$

$$\frac{\rho_2}{\rho_1} = \frac{(\gamma + 1)\mathrm{Ma}_s^2}{(\gamma - 1)\mathrm{Ma}_s^2 + 2} \qquad [17.2.21]$$

$$\frac{T_2}{T_1} = \frac{\left[\gamma\,\mathrm{Ma}_s^2 - \frac{\gamma - 1}{2}\right]\left[\frac{\gamma - 1}{2}\mathrm{Ma}_s^2 + 1\right]}{\frac{\gamma + 1}{2}\mathrm{Ma}_s^2} \qquad [17.2.22]$$

with

$$\mathrm{Ma}_s = u_1/a_1 \qquad [17.2.23]$$

where a is the velocity of sound, Ma is the Mach number and the subscript s is the shock wave.

A detailed discussion of the properties of the R–H curve is given by Kuo (1986).

17.2.5 Reactive shock wave

Moving on to modelling of a planar shock wave in a reactive medium, or detonation wave, the introduction of a heat input term q into Equation 17.2.7 gives

$$h_2 - h_1 - q = \frac{1}{2}(p_2 - p_1)(v_1 + v_2) \qquad [17.2.24]$$

where q is the energy addition per unit mass, or specific energy input, in the flow behind the shock front. As before, Equation 17.2.24 can be rewritten in the alternative form

$$\frac{\gamma}{\gamma - 1}(p_1 v_1 - p_2 v_2) - q = \frac{1}{2}(p_2 - p_1)(v_1 + v_2) \qquad [17.2.25]$$

As shown in Figure 17.1(b), this equation gives a family of R–H curves for $q = 0$ and for finite values of q.

17.2.6 Chapman–Jouguet model

Equation 17.2.24 is the basis of the Chapman–Jouguet (CJ) model. Equation 17.2.25 is an alternative form.

Figure 17.1(c) shows the regions of the R–H curve for a finite value of q. There are two broad regions. The first, where $p_2 > p_1$ and $v_2 < v_1$, is the region of detonation with a compression wave and the second, where $p_2 < p_1$ and $v_2 < v_1$, is the region of deflagration with a rarefaction wave. The combustion conditions along the curve pass from strong detonation, through weak detonation, then weak deflagration, to strong deflagration.

The CJ equation has not one but a set of solutions. The solution to which its authors came, namely that the velocity of the shock front is the minimum consistent with the conservation laws, is embodied in the CJ hypothesis that

$$a + u_2 = u_1 \qquad [17.2.26]$$

The CJ hypothesis may be explained by reference to Figure 17.1(d). The initial state of the gas is represented by the point O. Three possible final states are shown at S, W and J together with the lines OWS and OJ, the latter being the line of the tangent from O. In the region of S the sum of the velocity of sound and that of the gas exceeds the velocity of the front ($a + u_2 > u_1$) so that any rarefaction occurring in the flow behind the front tends to overtake and weaken it, and thus this state is unstable. The velocity of the front tends towards point J. In the region of W the sum of the velocity of sound and that of the gas is less than the velocity of the wave ($a + u_2 < u_1$) so that any energy release occurring in the flow behind the front is not available to sustain it, and thus this state also is unstable. Again the velocity of the front

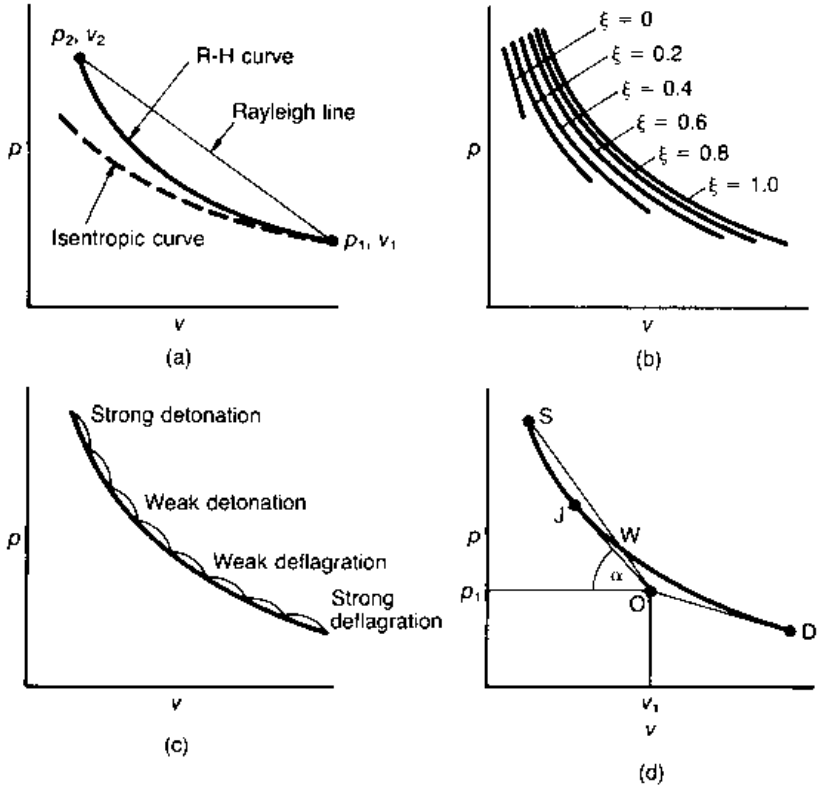

Figure 17.1 *Rankin–Hugoniot diagram: (a) R–H curve, isentropic curve and Rayleigh line; (b) family of R–H curves for different fractions ξ of completion of reaction; (c) detonation and deflagration regions of the R–H curve; and (d) the Chapman–Jouget state*

tends towards point J. Hence J is the only stable state in the detonation region. It can also be shown that in the deflagration region the only stable state is D, where the line OD is that of the tangent from O. Points J and D are known as the upper and lower CJ points.

The angle α of the line OJ is given by $\tan \alpha = (p_2 - p_1)/(v_1 - v_2)$ and from Equation 17.2.9

$$u_1 = v_1 \left(\frac{p_2 - p_1}{v_1 - v_2}\right)^{\frac{1}{2}} = v_1 (\tan \alpha)^{\frac{1}{2}} \qquad [17.2.27]$$

In this model the pressure p_2, the velocity u_1 and the Mach number Ma_1 are frequently referred to as the CJ pressure p_{CJ}, the CJ velocity u_{CJ} or D_{CJ} and the CJ Mach number Ma_{CJ}.

More detailed accounts of the full CJ model equations are given by B. Lewis and von Elbe (1987) and by Kuo (1986). The latter also gives a calculation scheme for the determination of the CJ parameters.

Work by von Neumann (1942) showed that at the instant when the front arrives there is a sharp, higher pressure, the von Neumann spike.

The shock wave profile yielded by the CJ model is illustrated in Figure 17.2. The shock wave travels as a sharp front. At the instant when the front arrives there occurs the von Neumann spike (point A). Very close to this in time is a lower pressure peak at the CJ plane

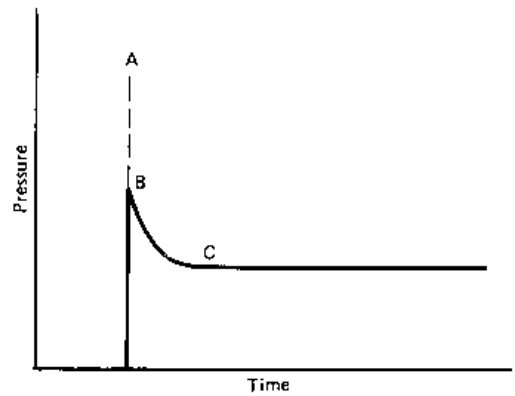

Figure 17.2 *Detonation front in a pipe: A, von Neumann spike; B, CJ peak; C, plateau pressure*

(point B). Following this the pressure decays to a plateau value (point C).

There are a number of relations which may be used to obtain approximate estimates of the CJ parameters. A very simple equation is the Zeldovich approximation (Zeldovich and Kompaneets, 1960) relating the CJ

pressure p_2 to the pressure p_v of constant volume combustion:

$$p_{CJ} \approx 2p_v \quad [17.2.28]$$

Another equation for the CJ pressure is that given by Weir and Morrison (1954):

$$\frac{p_{CJ}}{p_1} = \frac{1 + \gamma_1 \, Ma_{CJ}}{1 + \gamma_2} \quad [17.2.29]$$

The following approximate equations are given by Nettleton (1987):

$$p_2 \approx \frac{2q(\gamma_2 - 1)}{v_1} \quad [17.2.30]$$

$$\frac{\rho_2}{\rho_1} \approx \frac{\gamma_1 + 1}{\gamma_1} \quad [17.2.31]$$

$$u_1 \approx [2q(\gamma_2^2 - 1)]^{\frac{1}{2}} \quad [17.2.32]$$

These relations are applicable for $Ma_{CJ} \geq 4$, which for systems of interest is generally the case.

Some data of Strehlow on the specific heat input and ratio of specific heats γ for stoichiometric mixtures of various fuels for use in CJ model calculations are given by W.E. Baker *et al.* (1983). The data for ethylene are a specific heat input of 3.834 MJ/kg of the mixture and a ratio of specific heats of 1.188. The CJ pressure, temperature and velocity quoted, obtained from relations given by these authors rather than from those quoted above, are 18.63 bar, 2929 K and 1822 m/s, respectively.

The behaviour of detonation waves from combustion of hydrocarbon gases has been investigated by Burgess *et al.* (1968 BM RI 7196) in experiments in pipes up to 24 in. diameter.

An illustration of a detonation in a stoichiometric acetylene–air mixture is described in detail. The von Neumann spike pressure is 34 atm with an ignition delay time of 10^{-6} s. The decay from the von Neumann spike pressure to the CJ, or detonation, pressure of 19 atm occurs in about 10^{-5} s, giving an impulse of $(34 + 19)/2 \times 14.7 \times 10^{-5} = 4 \times 10^{-3}$ psi. The von Neumann spike is described as too fast to detect by instrumentation, but the CJ peak is detectable. The decay from the CJ pressure to the plateau pressure of 6.7 atm occurs in about 8.5 ms, giving an impulse of about 1.6 psi.s.

The experiments confirmed the Zeldovich approximation. Also, the experimental plateau pressure p_{pl} was about 40% of the CJ pressure:

$$p_{pl} \approx 0.4p_{CJ} \quad [17.2.33]$$

Equations are given for the calculation of the plateau pressure.

The CJ model is has proved relatively successful in predicting the detonation pressure, density and velocity in readily detonable mixtures in straight pipes.

Comparisons based on experimental data obtained by B. Lewis and Friauf (1930) for mixtures of hydrogen, oxygen and other gases have been widely quoted. Other work includes that of Berets, Greene and Kistiakowsky (1950) and D.G. Edwards, Williams and Breeze (1959). For a 2:1 mixture of hydrogen and oxygen the latter obtained the following values of the detonation parameters:

Pressure (atm)		*Velocity* (m/s)	
Observed	*CJ model*	*Observed*	*CJ model*
18.6	18.6	2825	2853

The observed pressure was the average pressure over 20–80 μs.

17.2.7 Zeldovich–von Neumann–Döring model

A weakness of the CJ model is the assumption that the chemical reaction which is the source of the heat release is infinitely fast. A further advance came with the development of a model which took account of the finite rate of reaction, and of heat release. The model was formulated independently by Zeldovitch (1940), von Neumann (1942) and Döring (1943), and is known as the ZND model. In this model there is no reaction immediately behind the shock wave and there is an incubation period before the reaction begins. The fractional completion of the reaction is characterized by the parameter ξ, and there is therefore a family of R–H curves for values of ξ between 0 and 1.

The ZND model is more realistic and provides a firmer basis for the development of unidimensional models. One particular use is in predicting the pressure–time profile of the detonation, including the von Neuman spike. For engineering predictions, however, it appears to be less used than the CJ model.

17.2.8 Taylor expansion wave

The product gases behind the CJ plane expand isentropically and accelerate, so that there is a distribution of particle velocities. This distribution was investigated by G.I. Taylor (1950). The Taylor expansion wave is another important feature of detonation models.

17.2.9 Deflagration and detonation

Some principal differences between deflagration and detonation have been listed by R. Friedman (1953):

Characteristic ratio	*Deflagration*	*Detonation*
u_1/a_1	0.0001–0.03	5–10
u_2/u_1	4–6 (acceleration)	0.4–0.7 (deceleration)
p_2/p_1	0.98 (slight expansion)	13–55 (compression)
T_2/T_1	4–16 (heat addition)	8–21 (heat addition)
ρ_2/ρ_1	0.06–0.25	1.7–2.6

17.2.10 Detonation wave structure

The account of detonation waves which has just been given is a simplified one. In particular, it does not take account of the unsteady and multidimensional features of such waves. In some cases, the detonation wave exhibits behaviour which results in pressures higher than those

predicted by unidimensional theories. A case in point is spinning detonation fronts. In certain media the detonation front passing down a tube exhibits a stable spin. A spinning detonation front may be characterized in terms of the wavelength λ of the spin, or ratio of the pitch p of the spin to the diameter d of the tube:

$$\lambda = p/d \qquad [17.2.34]$$

It has been shown by Fay (1952) that

$$\frac{p}{d} = \frac{\pi(\gamma_o + 1)}{\gamma_o k_n} \qquad [17.2.35]$$

where γ_o is the ratio of specific heats of the detonation products and k_n is a Bessel function derivative. The values of γ_o range between 1.2 and 1.4 and k_n has the value 1.841. Equation 17.2.35 may be reformulated as

$$\frac{p}{d} = \frac{\pi d}{a_o k_n} \qquad [17.2.36]$$

where a_o is the velocity of sound in the burned gas.

Experimental evidence indicates that in a spinning front, local pressure ratios occur which are in excess of those predicted by unidimensional theories. Pressure ratios as high as 160 have been obtained in some work.

Another, related behaviour is that of galloping detonation fronts. These show regular oscillations in the velocity of the leading front. The phenomenon appears to be an extension of that of spin occurring in mixtures too close to the limit of detonability for a single transverse front to be supported. The regular peak velocities can exceed the CJ velocity by up to 35%, and the peak pressures shows a similar enhancement. The overdriven phase can persist over the relatively extended length of 0.1 m.

In marginally detonable mixtures, detonations are multidimensional. Several different types of front have been identified. They include equilibrium fronts, which have both constant time-averaged properties and a regularly recurring structure; other fronts which have the first but not the second of these features; and transient fronts.

The spinning detonation front is now regarded as a limiting form of multidimensional front. The leading front consists of a number of bulges formed by Mach stems. There are a number of transverse waves orthogonal to the leading front which start at the depressions between the bulges and which reflect from each other and from the walls. There are reaction zones at the leading front and at the transverse waves.

17.2.11 Detonation wave cells

A gas detonation possesses a three-dimensional structure made up of 'cells'. A good deal of work has been done to characterize these cells and to relate to them the principal features of detonations.

Experimentally the cell structure may be studied from soot patterns formed on the inner surface of the tube. It is found that typically for a cell

$$S \approx 0.6 L_c \qquad [17.2.37]$$

where L_c is the length of the cell and S its width.

Related variables are the induction zone length L_i and the induction time τ_i. The induction zone length is the distance between the shock front and the reaction zone front and the induction time the interval between the passage of these two fronts, the relation between the two being

$$L_i = \tau_i \, \mathrm{Ma}_s \, a_o \qquad [17.2.38]$$

where a_o is the speed of sound in the mixture and Ma_s the Mach number of the shock wave.

With regard to the form of the relation between L_c and L_i, work by Vasiliev, Gavrilenko and Topchian (1972), and others, on fuel–oxygen mixtures indicates that

$$L_c = 10 n L_i \qquad 5 \le n \le 10 \qquad [17.2.39]$$

in other words $50L_i \le L_c \le 100L_i$, where n is a constant.

Nettleton (1987) describes the use for hydrocarbon–oxygen mixtures of the value

$$L_c \approx 50 L_i \qquad [17.2.40]$$

and for hydrocarbon–air mixtures, except acetylene, the value

$$L_c \approx 15 L_i \qquad [17.2.41]$$

The induction length L_i increases as tube diameter increases. Nikuradse (1933) has shown that in pipe flow the distance to the establishment of fully developed turbulence is about 60 diameters. A similar proportionality to diameter might be expected for the induction length. The question is discussed by B. Lewis and von Elbe (1987). The evidence is that the proportionality holds in some cases but not in others.

The cell width S is equivalent to the spacing of the transverse waves. For this spacing, Nettleton (1987) gives the following estimates for mixtures at atmospheric pressure: 1–10 mm for near stoichiometric fuel–oxygen mixtures; 10–100 mm for near stoichiometric fuel–air mixtures; and 0.1–1.0 m for lean fuel–air mixtures.

The cell length L_c is related to the critical diameter d_c for transmission of a detonation from a tube across an abrupt expansion. In a classic study, Zeldovich, Kogarko and Semenov (1956) found that d_c/L_i = constant for all the gases which they tested.

Further work on this feature has been done by Gvozdeva (1961) and Mitrovanov and Soloukhin (1964). Using acetylene–oxygen mixtures, the latter obtained the relationships

$$d_c = 13S \qquad \text{Circular tubes} \qquad [17.2.42a]$$

$$d_c = 10S \qquad \text{Planar channels} \qquad [17.2.42b]$$

Additional work includes that of D.H. Edwards, Thomas and Nettleton (1979), who have shown that the two results are equivalent and suggested that they are of general applicability to detonations.

D.C. Bull *et al.* (1982) have studied the cell length, and the factors influencing it, for a number of gases. For stoichiometric mixtures with air at atmospheric pressure they give the following values of L_c: methane 310 mm, ethane 54 mm, propane 46 mm, n-butane 54 mm, acetylene 9.2 mm, ethylene 24 mm and hydrogen 10 mm.

These authors also discuss the relevance of cell size. A planar detonation wave cannot propagate in a channel of width substantially smaller than the half-width of a cell. This feature is relevant to the quenching of detonations.

In the transition from a planar to a spherical detonation wave at an abrupt expansion there is a critical number of cell widths in the planar front to sustain the detonation. For a circular tube this number is 13.

Equation 17.2.42a is an alternative statement of this fact. This feature also is relevant to quenching.

There is a close connection between the cell size and the critical energy E_c for initiation of a spherical detonation. Thus, Zeldovich, Kogarko and Semenov (1956) give the relation

$$E_c \propto \Delta^3 \qquad [17.2.43]$$

where Δ is an induction length, which is related to the cell size.

In the transition from deflagration to detonation there is some indication that the critical turbulent length scales may be of the same order as detonation cell lengths and that systems of different reactivity have a rank order similar to that for cell sizes.

17.2.12 Detonability characteristics

The detonability of fuel–air mixtures is characterized in terms of detonability limits and ignition sources.

There has been some debate about the existence of detonation limits separate from flammability limits, as illustrated in the following comment by Burgess *et al.* (1968 BM RI 7196): 'A consensus has gradually developed that almost any gas mixture that is flammable is also detonable if initiated with a sufficiently strong ignition source.' The existence of separate detonability limits is now recognized.

Compilations of data on the flammability of fuels generally do not include detonation limits, although a considerable amount of data are available scattered in the literature.

There are certain features which cast a degree of uncertainty over detonation limits. One is the phenomenon of cool flames. Another is the existence of compounds which are capable of detonation in the absence of an oxidant. Further, a distinction is made in respect of detonation between confined and unconfined situations. Separate detonation limits are quoted for these two situations.

For detonation limits for confined situations measurements are made in tubes. Accounts of such work include those of Michels, Munday and Ubbelohde (1970) and Borisov and Loban (1977). The measurement of detonation limits in unconfined gas clouds is more difficult. Features of such work have included the use of a containment such as a balloon, a very high energy ignition source, and oxygen-enriched mixtures, the results being extrapolated back to the nitrogen content of air. Work in this area has been described by Benedick, Kennedy and Morosin (1970) and D.C. Bull, Elsworth and Hooper (1979a,b).

Table 17.5 from Nettleton (1980b) gives detonation limits for a number of fuels in air for confined and unconfined situations. The author's original table gives limits for a large number of compounds and also the limits for mixtures with oxygen. In general, the detonation limits of a particular fuel are narrower than its flammability limits, with the exception of compounds which can detonate in the absence of an oxidant.

There are a number of compounds which can detonate in the absence of an oxidant. One such substance is gaseous acetylene, and extensive precautions are necessary when handling it industrially. Other self-decomposing chemicals include ethylene at pressures in excess of 7 MPa, hydrogen peroxide and ozone. Information on such compounds is given by Bretherick (1985).

Nettleton suggests that any self-decomposing compound should be considered as possibly capable of detonation, but also adds that there is are no well-established example of unconfined detonation of a self-decomposing substance.

In view of the relative paucity of data on detonation limits, it is attractive to be able to derive them from the flammability limits. Some correlations have been given by Nettleton (1987) for both confined and unconfined detonations. For a number of fuels, which include alkanes and alkenes, he gives the following relations for the lower and upper limits of detonation in a confined situation. For mixtures with air

$$\log_{10} \phi_l = 1.08 \log_{10} \phi_{st} - 0.84 \qquad [17.2.44]$$

$$\log_{10} \phi_u = 1.06 \log_{10} \phi_{st} + 0.64 \qquad [17.2.45]$$

and for mixtures with oxygen

$$\log_{10} \phi_l = 0.60 \log_{10} \phi_{st} - 0.78 \qquad [17.2.46]$$

$$\log_{10} \phi_u = 1.13 \log_{10} \phi_{st} - 0.56 \qquad [17.2.47]$$

Table 17.5 *Some data on detonation limits in mixtures with air for confined and unconfined situations (after Nettleton, 1980b) (Courtesy of* Fire Prevention Science and Technology*)*

Compound	*Detonation limits* (%) *(confined tube)*		*(unconfined)*		*Flammability limits* (%)	
	Lower	*Upper*	*Lower*	*Upper*	*Lower*	*Upper*
C_2H_6	2.87	12.20	4.0	9.2	3.0	12.4
C_3H_8	2.57	7.37	3.0	7.0	2.1	9.5
C_4H_{10}	1.98	6.18	2.5	5.2	1.8	8.4
n-C_8H_{18}	1.45	2.85			0.95	
C_2H_4	3.32	14.70			2.70	36.0
C_3H_6	3.55	10.40	3.5	8.5	2.4	11.0
C_2H_2	4.20	50.0			2.5	80.0
C_6H_6	1.60	5.55			1.3	7.9
C_2H_5OH	5.1	9.8			3.3	19.0
H_2	18.3	58.9			4.0	75.0

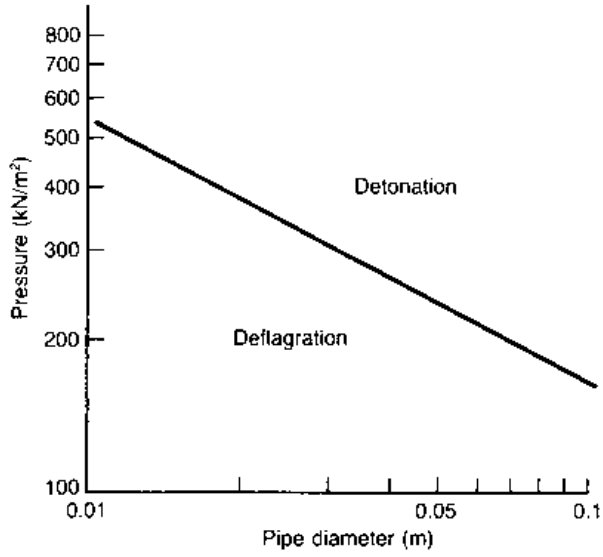

Figure 17.3 *Effect of pipe diameter and pressure on detonability of pure acetylene (after Sargent, 1957)*

where ϕ is the fuel–air ratio and the subscripts l, st and u denote the lower limit, stoichiometric and upper limit, respectively. The stoichiometric mixture is defined in terms of water and carbon dioxide as the products. For unconfined situations there is a single correlation for mixtures with air or with oxygen. This is

$$\log_{10} \phi_l = 0.51 \log_{10} \phi_{st} - 0.81 \quad [17.2.48]$$

$$\log_{10} \phi_u = 1.17 \log_{10} \phi_{st} + 0.60 \quad [17.2.49]$$

These correlations do not apply to acetylene, for which the detonation limits are wider.

Another approach to the prediction of detonation limits is in terms of homologous series.

There is relatively little information available on the influence of initial pressure and initial temperature on detonation limits, in confined situations. The general effect of an increase in initial pressure is to widen the detonation limits, and the same applies to an increase in initial temperature. The widening is more marked for the upper limit.

For acetylene, however, there exists a good deal of information on the effect of initial pressure. For this gas there is a pipe diameter below which only deflagration occurs, but above which detonation is possible, and this diameter is a function of the initial pressure. The correlation for this, which has been widely used in plant design, is shown in Figure 17.3. There is less information on the effect of initial temperature on acetylene, but at temperatures much in excess of 100°C there are likely to be present decomposition products which will affect the detonation limits.

The influence of additives, whether inert gases such as nitrogen or chemically active additives such as halohydrocarbons, presents a complex picture. The general effect of a diluent such as nitrogen is to narrow the detonation limits in air, particularly the upper limit. The amount of diluent required to suppress detonation tends to be large, but falls off sharply for mixtures close to the detonation limits. With regard to chemically active additives, the action of such additives may be rather specific, and there is some evidence, for example, that an additive effective as a fire extinguishant may not suppress a detonation.

The foregoing account has been concerned with the limits of detonation. However, whereas a mixture close to stoichiometric is, comparatively, readily detonable, one at the limits is detonation is only marginally detonable.

17.2.13 Initiation of detonation waves

The modes of initiation of a detonation differ somewhat from the modes of initiation of a deflagration. In both cases the process may be initiated by a suitable ignition source, but in the case of detonation other important mechanisms to be considered are initiation of a detonation by shock waves and acceleration of a deflagrative combustion into a detonation.

In the case of detonation, it is also necessary to consider the distinction already made between confined and unconfined situations.

A further relevant distinction is that between readily detonable and marginally detonable mixtures. It is by no means clear that the mechanisms of detonation in readily detonable media are those operating in marginally detonable media.

It is also necessary to bear in mind the evidence that detonation may be a stochastic process.

In treating detonation by an ignition source, it is usual to speak of strong and weak sources. The terms are convenient but often not well defined. Nettleton (1987) treats as strong those ignition sources which produce a shock or blast wave of velocity greater than the CJ

velocity, associated particularly with marginally detonable media and with unconfined systems. These strong ignition sources can range in strength from ≤ 10 J from sparks up to some 50 kJ from high explosives.

There is a considerable literature on the initiation of detonations in confined systems, but a large variety of methods have been used, and the interpretation of the findings is not straightforward. A greater degree of uniformity is now assisted by the adoption of standard methods, notably that of Zeldovitch and Kompaneets (1960). In this method a readily detonable mixture and a driving mixture are held in a tube separated by a diaphragm, which is removed seconds before detonation is initiated in the driving mixture. This technique allows the parameters of the driving mixture such as composition and initial pressure to be varied and the effect of the strength of the triggering wave to be investigated. The technique has been adapted to the study of unconfined detonations using an expansion nozzle.

Dealing first with initiation by ignition sources, for confined systems the quantity of interest is the minimum ignition energy for detonation. In principle, this is measured as a spark energy. However, data on this parameter are sparse and generally there is no alternative but to resort to the value of the regular minimum ignition energy (MIE), that for ignition of a flammable mixture.

A large amount of work has been done on initiation of detonation in unconfined vapour clouds by ignition sources such as sparks and high explosives. Here the ignition energy for detonation is generally expressed as the critical energy E_c for a spherical detonation. The critical energy E_c varies with the concentration of the fuel and has a minimum value E_c^*.

Work on spark initiation of detonation of unconfined clouds has shown that, as in similar work on ignition of flammable mixtures, the results obtained depend on factors such as the spark gap width and efficiency and the rate of energy deposition.

With regard to the strength of the explosive ignition source necessary to induce detonation, work by Bach, Knystautas and Lee (1971) has shown that for direct initiation of spherical detonation waves the rate of deposition of energy into the gas is critical. Reviewing this work, Strehlow (1973b) suggests that charge geometry is probably very important and that this factor may account for the apparent discrepancies in the quantities of explosive required to initiate detonation in the work which he quotes.

In considering the initiation of detonation in an unconfined cloud, the mechanism by which this occurs is of some relevance. It is now believed that when initiation occurs by a source with relatively low energy such as an electrical spark or 10 g of high explosive, the velocity of the initial blast wave decays below the CJ value before significant chemical reaction occurs in the flow, and there may be a propagation as quasi-steady state velocity before acceleration sets in again and leads to detonation. For the size of charge quoted, the distance over which this overall process occurs is of the order of 10 cm. For larger charges the distance is correspondingly greater, and may thus be appreciable.

Critical energies for initiation of spherical detonation have been obtained by a number of workers. Reviewing these, Nettleton (1987) quotes in particular data given by Carlson (1973) for mixtures of fuel and oxygen. The fuel concentrations in the most readily detonable mixtures lie in the range 20–40% and the values of the critical energy E_c obtained range over two orders of magnitude from <0.11 J for acetylene to 12.5 J for acetaldehyde. He comments that the chemical nature of the fuel strongly influences detonability but that the effect is more complex than one of simple bond strength.

The critical energy E_c for detonation in a spherical cloud is related to the critical diameter d_c for transmission of a detonation from a tube across an abrupt enlargement of area as described below. The determination of d_c therefore provides a mean of estimating E_c. Matsui and Lee (1979) use the relation

$$E_c = \frac{\pi p_D u_D}{24 c_D} d_c^3 \qquad [17.2.50]$$

where c is the velocity of sound, p is the absolute pressure and u is the particle velocity, and the subscript D denotes the detonation, or CJ, state.

These authors also give a detonation hazard parameter D_H, which they define as

$$D_H = \frac{E_c^*(\text{fuel})}{E_c^*(\text{acetylene})} \qquad [17.2.51]$$

where E_c^* is the minimum critical energy determined.

Work on the critical energy for detonation of fuel–air mixtures using high explosives has been described by D.C. Bull, Elsworth and Hooper (1979a). Figure 17.4 shows their results for the initiation of detonation in mixtures of ethane and air using charges of tetryl. As the graph shows, the mass m of explosive required to give initiation increases rapidly as the stoichiometric ratio λ diverges from the value for minimum critical energy.

A second mode of initiation of detonation in confined systems is by shock waves. This is amenable to study in shock tubes, and is thus a relatively well defined situation and has been widely investigated. A shock wave entering a flammable mixture compresses and heats it, typically creating hot spots. The mechanisms involved in the transition to detonation have been elucidated by Oppenheim and co-workers (Urtiew and Oppenheim, 1966, 1968; Lundstrom and Oppenheim, 1969), who found that intense reaction occurs in the highly turbulent region between the leading shock front and the flame, in effect an 'explosion within an explosion', so that the compression fronts created overtake and merge with the leading front, forming a detonation wave.

The third mode of initiation is acceleration of deflagration up to detonation, or 'run up'. Consideration is given first to the general phenomenon and then to run-up distances in confined and unconfined situations.

17.2.14 Deflagration to detonation transition

The deflagration to detonation transition (DDT) has been the subject of a considerable amount of work.

Considering first conditions in confined systems, elucidation of the mechanisms of the DDT in tubes owes much to the work of Oppenheim and co-workers. Accounts include those of Laderman, Urtiew and Oppenheim (1963), Urtiew and Oppenheim (1965, 1966, 1967) and Lundstrom and Oppenheim (1969).

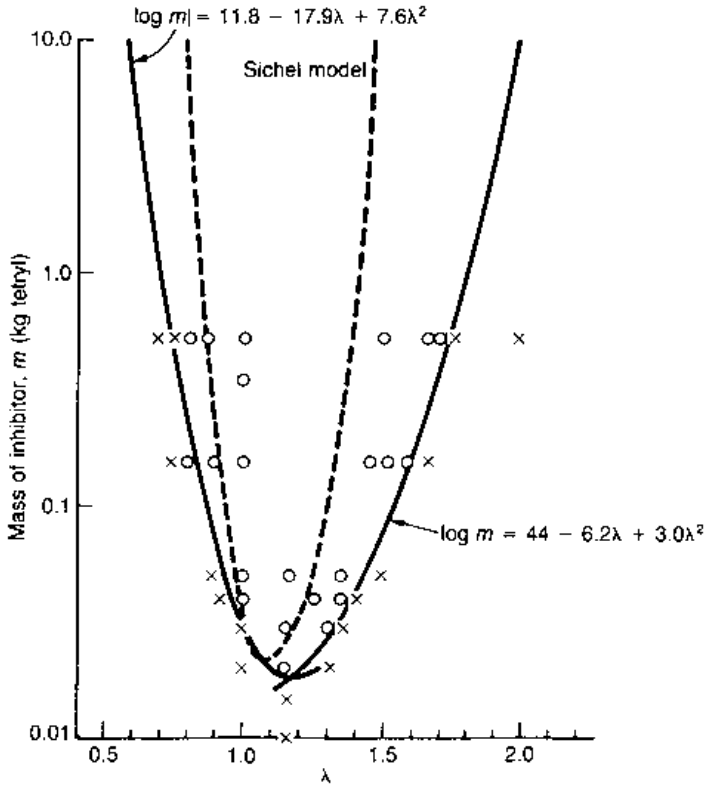

Figure 17.4 *Energy for initiation of explosion in ethane–air mixtures (D.C. Bull, Elsworth and Hooper, 1979a) (Courtesy of the Combustion Institute)*

If a flammable mixture is ignited at the open end of a pipe with the other end closed and if the pipe is of sufficiently small diameter for the flow of the unburned gas to be stabilized by viscous drag at the wall, the flame does not accelerate. Outside this laminar steady state regime, however, the propagation of the flame is always self-accelerating.

The flame acceleration is caused by a number of factors. As the flame moves down the pipe, the turbulent boundary layer grows until it occupies the whole cross-section of the pipe, so that there is a growth in turbulence. As the flame elongates, there is an increase in flame area. The flame creates pressure waves. There is precompression and preheating of the unburned gas ahead of the flame. Shock waves form and a turbulent flame brush is created. At some point, burnout of this turbulent flame brush occurs which intensifies the shock waves. These processes can be sufficient to cause the shock waves to coalesce and form a shock front and for this then to escalate into a detonation.

Another mechanism which can cause the DDT is the impact of a shock wave on the accelerating flame. Studies have been conducted by Markstein (1957) on the effect of the impact of a shock wave meeting a laminar flame head-on. These showed that a rarefaction wave travelled back through the unburned gas and a jet of unburned gas developed which penetrated deeply into the burned gas. The shear between the burned and unburned gas resulted in extreme turbulence and a massive increase in the burning rate. Such an effect may occur when a shock wave travels ahead of the flame and is then reflected back into it.

The sequence of events in the DDT is summarized by Kuo (1986) as follows: (1) an accelerating laminar flame, with flame wrinkling and compression waves; (2) formation of a shock front; (3) creation of a turbulent flame bush; (4) onset of an explosion within an explosion, with transverse waves; (5) development of a spherical shock behind the shock front; (6) interactions of the transverse waves with the shock front, retonation wave and reaction zone; (7) establishment of a steady wave, leading to a shock-deflagration ensemble, or detonation.

Kuo distinguishes four modes of transition, classified according to the location of the explosion within an explosion. Since generation of any particular pattern depends on minute inhomogeneities, the detailed sequence of events in the DDT is not reproducible.

17.2.15 Run-up distances in confined situations

There is a good deal of information on run-up distances for particular mixtures and pipes, but a general correlation has been lacking.

An attempt to remedy this deficiency has been made by Nettleton (1987), in terms of the distance X_s between

the origin of the flame and the position at which shock is produced. He gives for this

$$X_s = \beta(\gamma + 1)X_f \quad [17.2.52]$$

with

$$X_f = \frac{2c^2}{(\gamma + 1)^2 \beta^2 g_f} \quad [17.2.53]$$

$$g_f = f(\epsilon S_u) \quad [17.2.54]$$

where c is the speed of sound in the uncompressed gas, g_f is the acceleration of the flame, S_u is the maximum fundamental burning velocity, X_f is the distance from the origin of the flame to its position at the time at which the shock first forms, X_s is the distance from the origin to the position at which the shock is produced, β is the ratio of the velocity of the flow just ahead of the flame to that of the flame, γ is the ratio of specific heats of the reactants and ϵ is the expansion ratio. The value used for β is 0.9.

Nettleton gives a number of graphs comparing predictions of the distance X_s for shock formation with experimental values of the run-up distance X_d. The curves given by the model appear to have the general shape of, but do not always coincide with, the experimental ones. Specifically, the model predicts correctly the marked increase in run-up distance near the detonation limits.

It is suggested by Nettleton that if use is made of a run-up distance determined experimentally, this should be divided by a safety factor of 2 to allow for possible differences between the pipe used in the experiments and that on the plant.

With regard to the factors which influence the run-up distance, one of the most important is pipe diameter. Here there are a number of features which influence run-up but which vary with diameter. Thus, for example, in larger pipes the effect of viscous drag will be less but the surface roughness may be greater. It is clear from experiments that the run-up distance increases as the diameter increases, but the precise form of the relationship obtained varies. Nettleton quotes two sets of results, one in pipes of diameter $d \leq 102$ mm showing $X_d \propto d^{0.44}$ and one in pipes of $d \leq 51$ mm showing $X_d \propto d^{0.5}$, but states that there is general agreement that for large pipes $X_d \propto d$.

Another factor which affects the run-up distance is the surface roughness of the pipe. Essentially any feature which promotes turbulence will tend to reduce the run-up distance. Such features include internal welds and bellows.

There is relatively little information available on the influence on run-up distances of initial pressure, initial temperature or additives.

Attention is drawn by Nettleton to the fact that where pressure piling may occur, the probability of occurrence increases with the induction distance.

17.2.16 Run-up distances in unconfined situations

Turning now to acceleration of deflagration to detonation in unconfined systems, it is appropriate at this juncture to point out that the occurrence of a detonation in a vapour cloud which is truly unconfined has been a matter of some debate. The nature of, and models for, vapour cloud explosions are discussed in Section 17.28. Here consideration is confined to the process of flame acceleration in the cloud. This is closely linked to the question of the minimum size of cloud for a detonation to occur.

A model for the direct formation of a spherical detonation has been given by J.H.S. Lee and Moen (1980). This is the shock wave amplified coherent energy release (SWACER). The energy from the ignition source is assumed to create a gradient of temperature and of active species such that as the wave expands, each successive shell has a different induction time. Where there exists a suitable relation between this gradient and that of the decaying blast, the reaction zone couples to the leading front and a detonation wave forms.

There are certain features of combustion in a vapour cloud in the open which have been identified as possibly capable of promoting flame acceleration. One is heat radiation from the burning part of the cloud. It has been shown experimentally the heat flux can be such as to heat up incombustible particles ahead of the flame front so that they become ignition sources. Another is inhomogeneities in the cloud.

It is also of interest to know whether there is a minimum diameter d_{min} of a vapour cloud to support a detonation. Nettleton (1987) states that experience of deflagration in vapour clouds indicates that $d_{min} \geq 50$ m.

Moen, Donato *et al.* (1981), in work directed to the measurement of detonation limits, have studied the effect of tube diameter on the fuel concentration at the limit of detonability, which they take as the occurrence of single-head spin. They give results showing for ethylene–air mixtures the variation of the tube diameter for the transition from multiheaded detonation to single-head spin. They take the cell length L_c as proportional to the tube diameter, and express the correlation in terms of cell length also.

They then equate the above diameter to the critical diameter d_c and propose that this be taken as an indication of the minimum cloud diameter d_{min} for detonation. Thus for the stoichiometric concentration of 6.5% ethylene, they obtain $L_c = 46$ mm and, using Equations 17.2.37 and 17.2.42a, $S = 28$ mm and $d_c = 359$ mm $= 0.36$ m. Similarly for a 3% concentration they obtain $L_c = 0.9$ m, $S = 0.54$ m and $d_c = 7$ m.

17.2.17 Interaction between detonation and confinement

The foregoing has given an account of the general behaviour of detonations, essentially in tubes. It is now necessary to consider the interaction of a detonation wave with confinements in general.

There is no comprehensive theory for the interaction of a detonation wave with a confinement of arbitrary geometry. It is possible that a deterministic theory may be precluded by the stochastic properties already referred to.

The pressure profiles occurring in confined detonations have a number of characteristic features. The pressures generated exhibit wide variations in magnitude and duration. Anomalously high pressures can be generated by reinitiation of combustion in previously quenched regions of the gas.

Treatments of the interaction between a detonation wave and its confinement are mainly for non-reactive shock waves. Two principal theoretical descriptions are the two-shock theory and the method based on the work of Chester (1954), Chisnell (1957) and Whitham (1974), known as Chester–Chisnell–Whitham (CCW) analysis.

In general, theory in its current state is not able to predict peak local pressures or pressures on confining surfaces. But is helpful in understanding how interaction with confinements can result in fronts with properties different from those predicted by unidimensional models.

Models of a number of standard cases occurring with a confined detonation wave are treated by Nettleton (1987), using mainly CCW theory. These cases include (1) diffraction of a shock wave at an isolated wall, (2) normal reflection of a shock wave, (3) transmission of a detonation wave through an abrupt expansion and (4) propagation of a detonation through a bend or junction.

For diffraction at an isolated wall, the situation considered is a shock wave travelling parallel to a horizontal surface and then encountering another surface, or wall, at an angle θ_w to the horizontal. At some critical angle θ_{cr} there occurs transition to regular reflection. Three cases are treated: case 1, a wall at a negative angle with $\theta_w < 0$; case 2, a wall at positive angle less than the critical, hence $0 < \theta_w < \theta_{cr}$; and case 3, a wall at positive angle greater than critical but less than perpendicular, hence $\theta_{cr} < \theta_w < 90^\circ$.

Normal reflection of a detonation wave may occur in various configurations. These include reflection at a sharp 90° bend and at the wall of a spherical vessel. Essentially, the situation is that the use of unidimensional theory tends to overpredict the pressures generated, but that multidimensional theory is difficult to apply.

The transmission of a detonation wave through an abrupt expansion is a case of some importance. It constitutes a symmetrical, and therefore relatively simple, instance of a change from a planar front to a curved one and involves progression of the detonation from the pipe into a hemispherical detonation. It is therefore relevant to the critical diameter d_c of the pipe for the establishment of a hemispherical detonation and thus to the quenching of detonations and to the critical energy for the initiation of hemispherical detonations.

Nettleton gives a treatment of this case involving a combination of CCW analysis and Shchelkin (1959) instability theory.

He also describes a number of theoretical approaches to the derivation of a relation between the critical diameter d_c for quenching and the critical energy E_c for spherical detonation. Sloan and Nettleton (1975) have studied the case of a planar non-reactive shock wave emerging from a nozzle into a large space. Within the decaying shock envelope there exists a truncated cone, the front edge of which is travelling at the velocity of the incident front and which does work on the surrounding gas. A similar situation pertains for a detonation emerging from the nozzle. This case has been treated by Urtiew and Tarver (1981), who equate the work done with the critical energy. The work done W is

$$W = \int_0^{t_c} p u_{CJ} A_t \, dt \qquad [17.2.55]$$

where A_t is the area of truncation, p the pressure of the planar detonation, t_c the time at which the heads of the expansion fan cross the axis of symmetry and u_{CJ} the gas velocity behind the CJ front. But

$$t_c = \frac{L_c}{S} \frac{(d_c - d_o)/2}{D_{CJ}} \qquad [17.2.56]$$

where d is a diameter of the nozzle, D_{CJ} is the CJ velocity, L_c is the length of a detonation cell, S is the width of the cell, and the subscripts c and o denote critical and actual, respectively. Then, integrating Equation 17.2.55 using Equation 17.2.56 and noting that for spherical symmetry $E_c = 2W$

$$E_c = \frac{\pi p_{CJ} u_{CJ}}{4 D_{CJ}} \frac{L_c}{S} \left(\frac{d_c}{d_o} - 1 \right)^3 \qquad [17.2.57]$$

Equation 17.2.57 gives a relationship between the critical diameter d_c and the critical energy E_c. It has been shown by Nettleton (1987) that the equation gives a good fit to the data for mixtures of hydrocarbons with air and with oxygen obtained by Matsui and Lee (1979).

The propagation of a detonation through a bend is another case which is important but which has received rather less attention. There has been some success with CCW analysis of the early stages of the propagation of non-reactive shock waves round the bend, but rather less in the later stages as the process becomes more complicated due to interactions of wave systems set up at opposing walls.

Where the shock wave is in a reactive medium, the situation is yet more complex. Experimental work on detonation entering bends by Edwards, Nettleton and coworkers (D.H. Edwards *et al.*, 1981; D.H. Edwards, Thomas and Nettleton, 1983) has shown that steady detonation is re-established, but the distances at which re-establishment occurs and the locations of pressures higher than the CJ pressure depend on the configuration. Figure 17.5 by D.H. Edwards *et al.* (1981) shows a sketch from this work of a smoke–foil record of the re-establishment of a detonation in a sharp bend.

The patterns on, and damage to, the inner surface of such bends are characteristic, and thus in incident investigation may provide evidence of the occurrence of a detonation.

In addition to the interaction of a detonation wave with a confining envelope, the detonation wave may also interact with an adjacent gaseous medium. Some situations of interest are those where the adjacent medium is (1) an inert gas, (2) a gas mixture of uniformly decreasing concentration and (3) a gas mixture with concentration variations. The first case is relevant to any use of devices containing inert gas for the suppression of detonations. The other two cases have relevance to possible detonations in vapour clouds, which will in general have both concentration gradients and pockets of high and low concentration. Nettleton (1987) gives an account of some research findings which bear on these phenomena.

In the absence of an adequate treatment of the interaction between the detonation wave and its confinement, the common practice of comparing predicted pressures and static strength is likely to continue.

17.2.18 Damage caused by detonation to confinement

The treatment of the damage caused by detonations differs depending on whether the detonation is confined

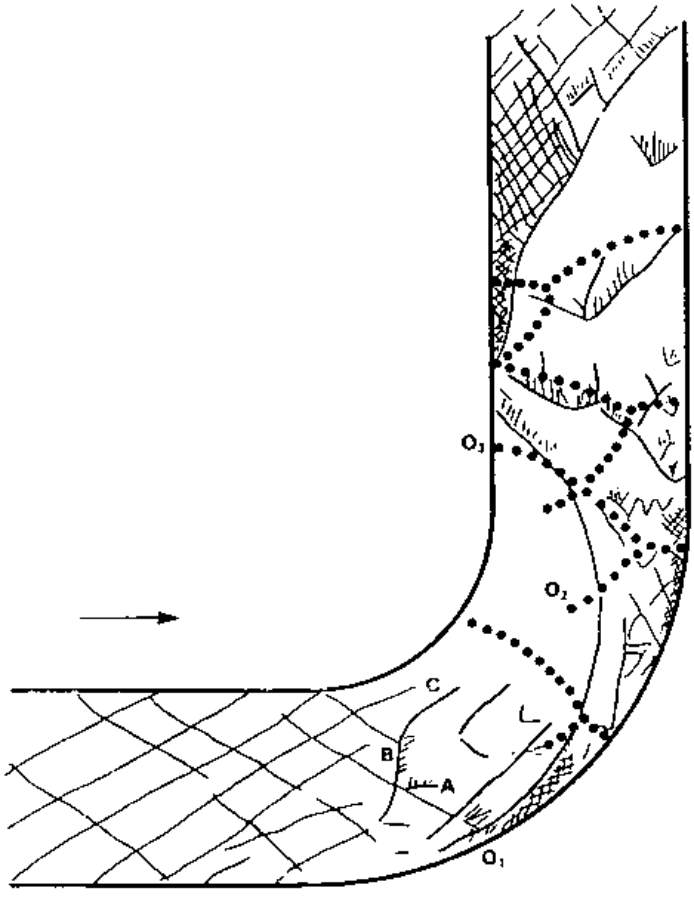

Figure 17.5 *Sketch of a smoke foil record of re-establishment of detonation in a sharp bend (D.H. Edwards et al., 1981). Steady front formed some diameters downstream of bend, following reflection of triple point, trajectory $O_1O_2O_3$, at inner wall; ●●●, shock profiles in reactive medium (Courtesy of* Archivum Combustionis*)*

or unconfined. The effects of explosions in the open, whether fast deflagrations or detonations, are considered in Sections 17.31–17.42. The account here is limited to confined detonations.

The general effects of confined detonations are evident from the explosions which have occurred inside plant over the years. A review has been given by Strehlow and Baker (1976). Accounts of some of these incidents are given in Appendix 1.

One classic case is the explosion at Whiting, Indiana, in 1955 described by Jacobs *et al.* (1957) and Randall *et al.* (1957) (Case History A22).

Generally, the amount of information which can be gleaned from an incident of detonation inside plant is limited, because crucial items of data are missing.

Two general points on damage caused by detonations may be noted. One is that the evidence indicates that the damage done by a dynamic loading is no greater than that which would be expected from the corresponding static loading. The other is that ductility appears to have little effect on the dynamic bursting pressure.

The present state of knowledge does not permit a fundamental prediction of the damage to plant by a detonation occurring in it. As already described, there is no comprehensive theory to support the reliable estimation of the pressures generated in complex plant. Further, understanding of the mechanisms and modes of damage caused by confined detonations is imperfect.

Some general guidance is provided by the work which has been done to determine the effective pressures generated in a detonation. C. Campbell, Littler and Whitworth (1932) carried out experiments in which a copper disc at the end of a tube was sheared by a detonation in the tube. They found that the pressure at which failure occurred was close to the CJ pressure. In other words, it was less than the pressure spike and less still than the reflected pressure.

Approaches to the prediction of the pressures occurring in a detonation have been described above. Then given an estimate of this pressure, an attempt may be made to estimate the damage either from theoretical models or experimental correlations.

It can be shown that the force exerted by a suddenly applied load of a duration much longer than the time constant of the object impacted can be up to twice that produced by the corresponding load slowly applied. This provides a general theoretical indication of the force which a detonation may be expected to exert.

The behaviour of the wall of a pipe as a detonation passes along it has been modelled, in terms of the acceleration, velocity and deformation, both elastic and plastic, of the wall. Some simplified models are given by Nettleton (1987), drawing on work such as that of Randall and Ginsburgh (1961) and de Malherbe *et al.* (1966).

17.3 Explosives

Although the properties, manufacture, handling, storage and transport of high explosives are outside the scope of this book, it is necessary to make some brief mention of them.

Accounts of explosives are given in *Explosives, Their Anatomy and Destructiveness* (C.S. Robinson, 1944), *The Science of High Explosives* (M.A. Cook, 1958), *Prevention of and Protection against Accidental Explosion of Fuel and Other Hazardous Mixtures* (E. Cohen, 1968) and *Detonics of High Explosives* (Johansson and Persson, 1970).

Explosives are relevant to loss prevention in two areas in particular. These are (1) estimation of effects of explosions and (2) control of manufacture, handling, storage and transport of explosive materials.

Many of the data available on explosions and their effects and many of the methods of estimating these effects relate to explosives. In particular, the methods developed for calculating the effects of explosions are based mainly on the high explosive trinitrotoluene (TNT).

The hazard of explosives has long been recognized, and an approach has been developed for their control. Some aspects of this approach are applicable in the chemical industry also.

Selected references on explosives are given in Table 17.6.

Table 17.6 *Selected references on explosives*

MoD, ESTC (n.d.); Upmann (1878); Berthelot (1892); Assheton (1930); Thomson (1941); Read (1942); T.L. Davis (1943); M. Meyer (1943); Lothrop and Handrick (1949); E. Fisher (1950, 1953a,b); Jarrett (1952, 1968); J. Taylor (1952); H. Watts (1954); Johansson, Persson and Selberg (1957); M.A. Cook (1958, 1960); Home Office (1958/7, 1972/3); Tomlinson (1958); US Army, Ordnance Corps (1958, 1960); Federoff (1960); ICI (1961); Deb, Evans and Yoffe (1962); M.H. Friedman (1963a,b); Langefors and Kihlstrom (1963); Urbanski (1964–, 1983); Freytag (1965); Lenz (1965); D. Levine and Boyars (1965); D. Price and Wehner (1965); Fordham (1966, 1980); Gould (1966); Ornellas, Carpenter and Gunn (1966); Department of the Army (1967); Ornellas (1967, 1968); R.F. Fletcher (1968); Kamlet and Jacobs (1968); Napadensky (1968); Roylance (1968); W.I. Taylor (1968); Wieberson *et al.* (1968); Dremin (1969); Fauquignon and Cheret (1969); Johansson and Persson (1970); Porzel (1972, 1974, 1980); R. Meyer (1973, 1977); Woolfolk and Ablow (1973); Darling (1974); Filler (1974); Lovold (1974); Sablon (1976); R.L. Allen (1977a); Gregory (1977); C.M. Anderson and Pakulak (1978); HSE (1978b); Medard (1979); Dupont Co. (1980); Short *et al.* (1981); Kuo and Summerfeld (1983); Urbanski (1983); C. Tayler (1986a); Yinon and Zitrin (1987); Ijsselstein and van Steen (1988); J.H. Johnson *et al.* (1988); Doherty *et al.* (1989); Ho and Fong (1989); Ho, Fong and Hamshere (1989); E. Meyer (1989); de Yong and Campanella (1989); Meyers and Shanley (1990); Moran (1992); NFPA (1992 NFPA 495); Twisdale *et al.* (1992); P.A. Davies (1993); Kohler (1993)

Initiation of explosives
Bowden (1949, 1953); Bowden, Stoke and Tudor (1947); Bowden *et al.* (1947); Bowden and Yoffe (1949, 1952, 1958); A.J.B. Robertson (1949); Kistiakowsky (1949); Bowden and Tabor (1954); Bowden and Thomas (1954); Johansson, Persson and Selberg (1957); Johansson, Lundborg and Sjölin (1962); Rindner (1968); Chaudhri (1976); Berger (1977); W.H. Andersen (1979); Bauer (1982); Bless (1982); Erikson (1982); Nellis, Seaman and Graham (1982); Vantine, Chan and Erickson (1982); Vorthman (1982); Ho (1992); P.A. Davies (1993); Raha and Chhabra (1993)
Sympathetic detonation: van Dolah (1966 BM RI 6903)

Explosives testing (*see* Table 8.1)

Fireballs from explosives
Jarrett (1952); Gayle and Bransford (1965); Rakackzy (1975); Stull (1977); Kovar *et al.* (1982); W.E. Baker *et al.* (1983); Gilbert, Lees and Scilly (1994e)
Fireballs from nuclear weapons: Glasstone (1962); Teller *et al.* (1968); Ramsey (1983)

Munitions, weapons
MoD, ESTC (n.d); Rohne (1895); Gurney (1943, 1944, 1946); Christopherson (1946); Mott (1947); Dunn and Stern (1952); E. Fisher (1953); Tomlinson (1958); G.I. Taylor (1963a,b); Lenz (1965); Pollard and Arnold (1966); Department of the Army (1967); I.G. Henry (1967); Held (1968, 1979, 1990, 1991); Roylance (1968); Draper and Watson (1970); Filler (1974); Karpp and Predebon (1974); SIPRI (1978); Kamlet and Finger (1979); G.E. Jones, Kennedy and Bertholf (1980); Grady (1982a,b); C.E. Anderson, Predebon and Karpp (1985); E. Hirsch (1986); Massa (1987); McCleskey (1988a–c, 1992); Burman (1989); Helwig, Klee and Hubner (1989); Jagusch (1989); Naz (1989)

17.3.1 Explosions of explosives

In an explosion caused by a high explosive the rate of energy release is particularly rapid, and the explosion has high shattering power, or 'brisance'.

A high explosive produces, therefore, a quite distinct type of explosion. The shock wave from such an explosion has a very short duration time. Differences in the types of explosion are a weakness in the application of correlations based on explosions of high explosives to other explosion situations.

Nevertheless, the TNT equivalent model is widely used in explosion calculations for estimating the effects of explosion on process plant.

17.3.2 Scaling laws

The effects of the explosion of a high explosive are generally determined using a scaling law. A principal parameter which characterizes an explosion is its overpressure. The overpressure generated by the explosion of a explosive is discussed in detail in Section 17.25. It is shown there that overpressure p^o is a function of scaled distance z:

$$p^o = f(z) \qquad [17.3.1]$$

with

$$z = \frac{r}{W^{\frac{1}{3}}} \qquad [17.3.2]$$

where p^o is the peak overpressure, r is the distance, W is the mass of explosive and z is the scaled distance. Equation 17.3.2 implies that for a given overpressure the distance is related to the mass of explosive by a cube root law:

$$r \propto W^{\frac{1}{3}} \qquad [17.3.3]$$

Damage done by the explosion of an explosive may be correlated in terms of damage circles within which defined degrees of damage occur. The radius R of such a damage circle is related to the mass W of explosive approximately by a cube root law:

$$R \propto W^{\frac{1}{3}} \qquad [17.3.4]$$

Another effect of an explosion of a high explosive is the formation of a crater. A cube root law applies to the relation between the radius r_c of the crater and the mass W of explosive:

$$r_c \propto W^{\frac{1}{3}} \qquad [17.3.5]$$

In the storage of explosives the limit of distance between one store of explosive and the next is set by the risk of sympathetic detonation. A mean detonation distance r_{50} can be defined at which there is a 50% chance of sympathetic detonation occurring. It is found that this mean detonation distance r_{50} is related to the mass W of explosive by a cube root law:

$$r_{50} \propto W^{\frac{1}{3}} \qquad [17.3.6]$$

17.3.3 Housing damage

A scaling relation for blast damage to housing has been given by Jarrett (1968):

$$R = \frac{kW^{\frac{1}{3}}}{\left[1 + \left(\frac{7000}{W}\right)^2\right]} \qquad [17.3.7]$$

where R is the distance (ft), W the mass of explosive (lb) and k a constant. The constant k defines the degree of damage which may be expected to the average British dwelling house. It is based on the analysis of damage in 24 well documented explosions and in wartime bombing. The following categories of damage are defined:

		k
A	Almost complete demolition	9.5
B	50–75% external brickwork destroyed or rendered unsafe and requiring demolition	14
Cb	Houses uninhabitable–partial or total collapse of roof, partial demolition of one to two external walls, severe damage to load-bearing partitions requiring replacement	24
Ca	Not exceeding minor structural damage, and partitions and joinery wrenched from fittings	70
D	Remaining inhabitable after repair–some damage to ceilings and tiling, more than 10% window glass broken	140

17.3.4 Quantity–distance relations

In the handling of explosives separation distances are governed by quantity–distance relations. An account of the quantity–distance relations used in Britain has been given by Jarrett (1968).

The principal explosion effects of the different categories of explosive are:

Category X	Missiles and slight blast effects, projected ammunition
Category Y	Radiant heat
Category Z	Missiles and major blast effects, cratering, earth shock
Category ZZ	Major blast effects, cratering, earth shock

The quantity–distance relations are used for (1) storage distances, (2) process building distances, and (3) public building and traffic distances. The process building distances are also known as intraline distances.

The storage of explosives involves the hazard of explosion of the stored material. Explosives tend to be sensitive to shock. They also tend to deteriorate in storage. In particular, there is the hazard of sympathetic detonation of one store of explosives by another adjacent store.

Although sympathetic detonation is important, it is not the only explosion effect which has to be taken into account. Other effects include flame spread, heat radiation, missiles and blast. Jarrett quotes a number of quantity-distance relationships of the general form

$$R = kW^n \qquad [17.3.8]$$

where R is the distance, W is the mass of explosive, k is a constant and n is an index. The index n lies in the range $\frac{1}{3}$ to $\frac{1}{2}$.

For storage distances for category Z explosive in shells filled with RDX/TNT explosive the basis of separation is sympathetic detonation. For this case Jarrett gives the relation

$$R = 12W^{\frac{1}{3}} \qquad [17.3.9]$$

where R is the distance (ft) and W the mass of explosive (lb).

For intraline and public buildings distances for category Y explosive the basis of separation is heat radiation. For these cases the relations given by Jarrett are, respectively,

$$R = 8W^{\frac{1}{3}} \qquad [17.3.10]$$

and

$$R = 3.2W^{\frac{1}{2}} \qquad W < 10\,000 \qquad [17.3.11a]$$

$$R = 16W^{\frac{1}{3}} \qquad W > 10\,000 \qquad [17.3.11b]$$

For intraline and public building distances for category Z explosive the basis of separation is blast effects. The relevant relation is Equation 17.3.7.

17.3.5 Sympathetic detonation

Explosives are normally stored in separate stacks with a separation distance between each stack so as to reduce the probability of detonation of one stack as a result of detonation of an adjacent one. The effect is known as sympathetic detonation.

.A model for the propagation of an explosion by sympathetic detonation has been described by Masso and Rudd (1968). The blast effect B is assumed to be given by the relation

$$B = \frac{kW^{n_1}}{r^{n_2}} \qquad [17.3.12]$$

where B is the blast effect, r is the distance, W is the mass of explosive, k is a constant and n_1 and n_2 are indices. The probability p of further detonation of the pressure-sensitive material is taken as

$$p = B/B^* \qquad [17.3.13]$$

where B^* is the blast effect required for certainty of detonation. Then a general model for propagation of detonation is

$$p = 0 \qquad p' < T \qquad [17.3.14a]$$

$$p = p' \qquad T < p' < 1 \qquad [17.3.14b]$$

$$p = 1 \qquad \text{Otherwise} \qquad [17.3.14c]$$

with

$$p' = \frac{kW^{n_1}}{B^* r^{n_2}} \qquad [17.3.15]$$

where T is the threshold of p' below which no propagation occurs.

The simplest model described by the authors consists of a linear array of explosive components in n sites. The probability that the detonation reaches the jth site but does not continue to the $(j+1)$th site is as follows. The component of the initiating site detonates with certainty. The probabilities of detonation of components in the second, third and jth sites are p, p^2, ..., p^{j-1}. If the component at the jth site has detonated, the probability that at the $(j+1)$th site does not detonate is $(1-p)$. This yields the following relation:

$$P(j) = (1-p)p^{j-1} \qquad 1 \le j \le (n-1) \qquad [17.3.16a]$$

$$P(j) = p^{j-1} \qquad j = n \qquad [17.3.16b]$$

where $P(j)$ is the probability that j sites are involved in the detonation chain.

Various more complex models are also given by these authors.

17.3.6 Controls on explosives

The explosives industry has no choice but to exercise the most stringent controls to prevent explosions. Some of the basic principles which are applied in the management of hazards in the industry have been described by R.L. Allen (1977a). There is an emphasis on formal systems and procedures. Defects in the management system include:

> A defective management hierarchy ... Inadequate establishments ... Separation of responsibilities from authority, and inadequate delegation arrangements ....
> Inadequate design specifications or failures to meet or to sustain specifications for plants, materials and equipments.
> Inadequate operating procedures and standing orders ....
> Defective cataloguing and marking of equipment stores and spares ....
> Failure to separate the inspection function from the production function ....
> Poor inspection arrangements and inadequate powers of inspectorates ....
> Production requirements being permitted to over-ride safety needs ....

The measures necessary include:

> The philosophy for risk management must accord with the principle that, in spite of all precautions, accidents are inevitable. Hence the effects of a maximum credible accidents at one location must be constrained to avoid escalating consequences at neighbouring locations ....
> Siting of plants and processes must be satisfactory in relation to the maximum credible accident ....
> Inspectorates must have delegated authority – without reference to higher management echelons – to shut down hazardous operations following any failure pending thorough evaluation ....
> No repairs or modifications to hazardous plants must be authorized unless all materials and methods employed comply with stated specifications ....
> Components crucial for safety must be designed so that malassembly during production or after maintenance and inspection is not possible ....
> All faults, accidents and significant incidents must be recorded and fed back without fail or delay to the Inspectorate ....

A fuller checklist is given by Allen.

R.L. Allen (1977b) also discusses the relevance of these principles to the chemical industry, and to Flixborough in particular. He suggests that the probability of such accidents can be greatly reduced if the chemical industry uses these well proved methods. The principles are essentially those described elsewhere in this book.

In addition to these basic management aspects, the special precautions necessary in the manufacture and storage of explosives are instructive in relation to process plant hazards. Here some basic principles are (1)

minimization of inventory, (2) minimization of exposure, (3) use of blast walls and (4) separation by distance.

In explosives manufacture and storage the scale of the potential accident is reduced by minimizing the inventory of material and the number of people. The application of these concepts to process plant is discussed in Chapters 11 and 20.

Much use is made in the explosives industry of blast walls, cubicles and barricades. An account of their design has been given by Callahan (1968).

The only completely reliable protection with explosives, however, is distance. It is normal practice, therefore, to allow generous distances in both manufacture and storage. The principle of separation is applicable to process plant also, as described by Chapter 10, although it should be added that it does not necessarily follow that it is economically justifiable to require separation to be such as to give absolute protection.

There is much to learn from the explosives industry in managing the hazards on process plant, but, as always, methods developed for a similar, but not identical, problem need to be adapted to the needs of the process industries.

17.4 Explosion Energy

As already stated, an explosion is a sudden and violent release of energy. Discussions of explosion energy are given in the *High Pressure Safety Code* (B.G. Cox and Saville, 1975) and by Kinney (1962), Kinney and Graham (1985), Burgess *et al.* (1968 BM RI 7196), Eisenberg, Lynch and Breeding (1975), W.E. Baker *et al.* (1983), Crowl (1991, 1992a,c) and the Center for Chemical Process Safety (CCPS) (1994/15).

The energy released in an explosion on a process plant is normally one of the following: (1) chemical energy, (2) fluid expansion energy and/or (3) vessel strain energy.

The distribution of energy between the blast wave and missiles and any crater formation needs also to be considered as does the effect of the height above ground at which the explosion occurs.

17.4.1 Chemical energy

In considering the energy release in a chemical explosion, it is convenient to consider first condensed phase explosives, or high explosives, and then flammable gases and liquids.

The energy release in a chemical explosion is a function of the nature and state of the reactants and of the products. In general, the explosion products are not well defined. As the gas mixture cools, the chemical equilibrium shifts and the transient products disappear.

A condensed phase explosive contains its own oxygen so that it can explode even in the absence of air. It is conventional to assume certain nominal products of explosion. Explosives may be classified on the basis of nominal oxygen distribution. An oxygen-rich explosive has excess oxygen and the nominal products contain molecular oxygen and incombustible gases such as CO_2 and H_2O. An oxygen deficient explosive gives combustible gases such as CO and H_2 among the nominal products. The actual gases generated by explosives contain a mixture of all these products.

A flammable organic gas or vapour which explodes in excess air is normally assumed to yield incombustible gases such as CO_2 and H_2O. The same applies to a condensed phase explosive which undergoes combustion in excess air.

The quantities which characterize a high explosive are discussed by Kinney and Graham (1985). Those of interest here are (1) the energy of explosion, (2) the heat of explosion and (3) the heat of combustion.

The energy in an explosion is of two different kinds: (1) thermal energy and (2) work energy. That part of the energy transferred due to temperature difference is termed the heat of explosion.

The differences between the heat of explosion, the energy of explosion and the heat of combustion may be explained by reference to the methods by which they are measured for an explosive, as described by Kinney and Graham. The heat of combustion is determined by causing the substance to burn in air in a bomb calorimeter and measuring the heat evolved.

The heat of explosion is determined in a similar manner, but using inert gas instead of air. The substance is placed in a bomb calorimeter, air is replaced with inert gas, the substance is initiated and the heat evolved is measured.

Measurement of the energy of explosion is carried out by encasing the substance in a heavy sheath of metallic gold. The explosion flings the gold casing against the bomb wall, where it gives up its kinetic energy as heat, so that in this case the heat measured now includes this energy as well as that transferred by temperature difference.

The relative magnitude of these quantities may be illustrated by considering the values for TNT as given by Kinney and Graham (1985):

Heat of combustion $= 15\,132\,\mathrm{J/g}$

Energy of explosion $= 4850\,\mathrm{J/g}$

Heat of explosion $= 2710\,\mathrm{J/g}$

The heat of explosion corresponds to the internal energy change for the explosion ΔE.

In order to estimate the effects of an explosion it is necessary to know the energy of explosion. This is the work energy, or work. This work is done by the expansion of the gas and is given by

$$W = -\int_1^2 P\,\mathrm{d}V \qquad [17.4.1]$$

where P is the absolute pressure, V is the volume and W is the work of expansion. This is the energy transferred in the explosion as work done on the blast wave and missiles. The integral of Equation 17.4.1 is difficult to evaluate, and it is more convenient to work directly in terms of the initial and final values of the thermodynamic properties. The quantity generally used is the Helmholtz free energy change ΔA:

$$-\int_1^2 P\,\mathrm{d}V \approx \Delta A \qquad [17.4.2]$$

Treatments of the relationship between the work and the Helmholtz free energy change are given by Kiefer, Kinney and Stuart (1954) and W.J. Moore (1962).

The actual energy released in an explosion tends to be somewhat less than the Helmholtz free energy change. One reason is that the process is not reversible. Another is that the products of combustion of the explosion are usually at a temperature higher than ambient.

Often data are not available on the Helmholtz free energy change for a compound, but are available for the Gibbs free energy change. For many substances, including hydrocarbons, the difference is not great and the error involved in using the Gibbs instead of the Helmholtz free energy is small.

The following thermodynamic relations, which apply to a reversible process at constant temperature and pressure, are useful in explosion calculations. For absolute quantities

$$H = E + PV \qquad [17.4.3]$$

$$A = E - TS \qquad [17.4.4]$$

For isothermal change in a system

$$\Delta H = \Delta E + \Delta(PV) \qquad [17.4.5]$$

$$\Delta A = \Delta E - T\,\Delta S \qquad [17.4.6]$$

$$\Delta F = \Delta H - T\,\Delta S \qquad [17.4.7]$$

where ΔA is the Helmholtz free energy change, ΔE is the internal energy change, ΔF is the Gibbs free energy change, ΔH is the enthalpy change, ΔS is the entropy change and T is the absolute temperature.

The energy of explosion is usually calculated at standard conditions of 25°C and atmospheric pressure.

The internal energy change for the explosion reaction is

$$\Delta E = (\Delta E_f^o)_p - (\Delta E_f^o)_r \qquad [17.4.8]$$

where the superscript o denotes the standard state and the subscripts f the formation value, p the products and r the reactants, respectively. The enthalpy change for the reaction is

$$\Delta H = (\Delta H_f^o)_p - (\Delta H_f^o)_r \qquad [17.4.9]$$

The entropy change for the explosion reaction, or entropy of explosion, is

$$\Delta S = (S)_p - (S)_r \qquad [17.4.10]$$

The Helmholtz free energy change ΔA for the explosion reaction is given by Equation 17.4.6, or alternatively by

$$\Delta A = (\Delta A_f)_p - (\Delta A_f)_r \qquad [17.4.11]$$

For the entropy and Helmholtz free energy per mole of the reactants and products, assuming ideal gases,

$$S = S^o - R \ln p \qquad [17.4.12]$$

$$A = A^o + RT \ln p \qquad [17.4.13]$$

where R is the universal gas constant. For liquids and solids, the second term on the right-hand side of Equations 17.4.12 and 17.4.13 is negligible.

The Helmholtz free energy change may be calculated from thermodynamic data in several ways. One is to calculate ΔE from Equation 17.4.8 and ΔS from Equation 17.4.10 using Equation 17.4.12 to obtain S, and then to calculate ΔA from Equation 17.4.6. Alternatively, ΔA may be calculated from Equation 17.4.11, using Equation 17.4.13 to obtain ΔA_f.

The entropy term $T\Delta S$ is significant where there is a large difference between the number of moles of the reactants and of the products. This is the case for condensed phase explosives, but usually not for flammable gases and vapours. Where the change in the number of moles is not significant

$$\Delta A \approx \Delta E \qquad [17.4.14]$$

The enthalpy change may also be written as

$$\Delta H = \Delta E + \Delta n\,RT \qquad [17.4.15]$$

where Δn is the change in the number of moles. Where the change in the number of moles is not significant.

$$\Delta H \approx \Delta E \qquad [17.4.16]$$

Thus for explosions of flammable gases and vapours it is often possible to make certain approximations which simplify the task of obtaining the necessary data on thermodynamic properties.

For the explosive combustion of hydrocarbon clouds the method generally used is to determine the enthalpy change ΔH, which is usually obtained from the heat of combustion ΔH_c, and to apply to this an 'explosion efficiency', or yield factor, as discussed below.

The enthalpy change of the reaction ΔH may be calculated from the standard enthalpies of formation using Equation 17.4.9. Alternatively, it may be obtained from the heat of combustion.

If the heat of combustion is that of a gas and if the final water product is also gaseous, then the enthalpy change for the reaction is equal to the heat of combustion. Generally, however, the heat of combustion is given for a final water product which is a liquid. In this case the standard heat of combustion with liquid water product ΔH^o_{clw} should be corrected by a term which allows for the latent heat of vaporization of water ΔH_{vw} to give the standard heat of combustion with water product as vapour ΔH^o_{cvw}.

$$\Delta H^o_{cvw} = \Delta H^o_{clw} + n_w \Delta H_{vw} \qquad [17.4.17]$$

where ΔH_{cvw} is the heat of combustion with the final water product as vapour, ΔH_{clw} is the heat of combustion with the final water product as liquid, ΔH_{vw} is the latent heat of vaporization of water and n_w is the number of moles of water. This correction is usually of the order of 5–10% for hydrocarbons.

Sometimes the heat of combustion is given for a liquid rather than a gas. In this case the standard heat of combustion for a liquid ΔH^o_{cl} should be corrected by a term which allows for the latent heat of vaporization of the liquid ΔH_v to give the standard heat of combustion for the vapour:

$$\Delta H^o_{cv} = \Delta H^o_{cl} - \Delta H_v \qquad [17.4.18]$$

where ΔH_{cl} is the heat of combustion with initial reactant as liquid, ΔH_{cv} the heat of combustion with initial reactant as vapour and ΔH_v the latent heat of vaporization.

As an illustration of the calculation of the energy of explosion of an explosive, consider the calculation of the energy of explosion of TNT in the absence of air.

Following Kinney (1962) the explosion reaction is assumed to be

$$C_7H_5O_6N_3 \rightarrow C + 6CO + 2.5H_2 + 1.5N_2 \qquad [17.4.19]$$

The thermodynamic data are

	ΔE_f^o (kcal/mol)	S^o (cal/mol K)
$C_7H_5O_6N_3$	−13.0	65
C	0	1.361
CO	−26.722	47.301
H_2	0	31.211
N_2	0	45.767

The molecular weight of TNT is 227.

Then the internal energy of explosion from Equation 17.4.8 is

$$\Delta E = (\Delta E_f^o)_p - (\Delta E_f^o)_r$$

$$= \{(1 \times 0) + [6 \times (-26.722)] + (2.5 \times 0)$$

$$+ (1.5 \times 0)\} - [1 \times (-13.0)]$$

$$= -147.3 \text{ kcal/mol}$$

$$= -147\,300 \text{ cal/mol}$$

$$= -147\,000/227$$

$$= -649 \text{ cal/g of TNT}$$

The entropy of explosion from Equations 17.4.10 and 17.4.12 is

$$\Delta S = (S^o - R \ln p)_p - (S^o)_r$$

The entropy of mixing terms are:

	p	$-R \ln p$
CO	0.6	1.016
H_2	0.25	2.753
N_2	0.15	3.767

Then the entropy of explosion is

$$\Delta S = \{(1 \times 1.361) + [6 \times (47.301 + 1.016)] + [2.5 \times (31.211 + 2.753)] + [1.5 \times (45.767 + 3.767)]\} - (1 \times 65)$$

$$= 385.5 \text{ cal/mol K}$$

Hence the energy of explosion from Equation 17.4.6 is given by

$$\Delta A = \Delta E - T\,\Delta S$$

$$= -147\,300 - (298 \times 385.5)$$

$$= -262\,180 \text{ cal/mol}$$

$$= -262\,180/227$$

$$= -1155 \text{ cal/g of TNT}$$

The experimental value of the energy of explosion of TNT is quoted by Kinney as 1120 cal/g. Kinney gives an alternative calculation which utilizes instead Equations 17.4.11 and 17.4.13, but gives an identical result.

Other values of the energy of explosion of TNT have been discussed by Burgess *et al.* (1968 BM RI 7196).

An alternative explosion reaction without air given by Ornellas (1967) is

$$C_7H_5O_6N_3 \rightarrow 3.7C + 2CO + 1.3CO_2 + 0.1CH_4 + 0.5H_2 + 1.6H_2O + 1.3N_2 + 0.2NH_3 \qquad [17.4.20]$$

For this reaction the energy of explosion given is 1093 cal/g.

If the combustion of TNT takes place in the presence of excess air, the conventional explosion reaction is

$$C_7H_5O_6N_3 + O_2(\text{excess}) \rightarrow 7CO_2 + 2.5H_2O + 1.5N_2 \qquad [17.4.21]$$

For this reaction the energy of explosion, or rather combustion, given is 3600 cal/g.

The energy of explosion of TNT is widely utilized as a reference value. The energy used is normally that for explosion in the absence of air. The value of this energy of explosion which is used here is 1120 cal/g of TNT, as given by Kinney.

As an illustration of the calculation of the enthalpy change in the explosion of a flammable gas, consider the calculation of that for an acetylene–air mixture. The explosion reaction is assumed to be

$$C_2H_2 + 2.5O_2 \rightarrow 2CO_2 + H_2O \qquad [17.4.22]$$

The thermodynamic data are

	ΔH_f^o (kcal/mol)
C_2H_2	54.194
O_2	0
CO_2	−94.052
H_2O (g)	−57.798

Then the enthalpy change for the explosion from Equation 17.4.9 is

$$\Delta H = (\Delta H_f^o)_p - (\Delta H_f^o)_r$$

$$= \{[2 \times (-94.052)] + [(1 \times (-57.798)]\}$$

$$-[(1 \times 54.194) + (2.5 \times 0)]$$

$$= -300.096 \text{ kcal/mol}$$

Alternatively, the heat of combustion may be used. The standard heat of combustion of acetylene is

$$\Delta H_{clw}^o = -310.615 \text{ kcal/mol}$$

This value is for acetylene gas, so no correction is required for the state of the reactant, but the value assumes that the final water product is liquid. The latent heat of water is

$$\Delta H_{vw} = 9.7 \text{ kcal/mol}$$

Table 17.7 *Characteristics of four combustion processes for acetylene in air*[a,b] *(After Burgess* et al.*, 1968 BM RI 7196)*

	Final pressure (atm)	*Final temperature* (K)	$-\Delta$H (cal/g of initial mixture)
Bomb calorimeter	1	298	842
Open flame	1	2537	692
Constant volume explosion	9.78	2918	630
Detonation	19.56	3230	550

[a] The legend to the authors' table refers to 'stoichiometric acetylene–air'
[b] The original table gives the heat released in terms of the enthalpy change ($-\Delta H$), as shown here. The heat released at constant pressure, as in the open flame case, is an enthalpy change, that released at constant volume, as in the bomb combustion cases, is an internal energy change.

Hence the corrected standard heat of combustion of acetylene is

$$\Delta H^{\circ}_{\text{cvw}} = -310.615 + 9.7$$

$$= -300.915 \text{ kcal/mol}$$

ΔH is then equal to this value of $\Delta H^{\circ}_{\text{c}}$ and agrees well with that calculated earlier.

These methods of calculating the energy of explosion of flammable gases and vapours are those which are normally used for industrial explosion calculations.

The foregoing methods assume that the hot product gases are cooled back to standard conditions. The effect on the enthalpy change in the explosion of assuming other termination conditions is illustrated by the calculations given by Burgess *et al.* (1968 BM RI7196) for the combustion of a stoichiometric acetylene–air mixture. Some cases are considered in Table 17.7. For the bomb calorimeter the final mixture composition is CO_2 16.1%, H_2O 8.1% and N_2 75.8%, but for the other cases there are other products present such as CO, H_2, O, H and OH.

Calculations of this kind are relevant to the estimation of the energy available in explosion processes in process plant and pipelines.

There are available extensive tabulations of thermodynamic properties at standard conditions (25°C, atmospheric pressure). Tabulations of thermodynamic properties are given in National Bureau of Standards (NBS) Circular 461 *Selected Values of Properties for Hydrocarbons* (1947), NBS Circular 500 *Selected Values of Chemical Thermodynamic Properties* (1952) and NBS Circular 270–3 *Selected Values of Chemical Thermodynamic Properties* (1969), in the NBS *JANAF Thermochemical Tables* (Stull and Prophet, 1971) and in American Petroleum Institute (API) Research Project 44 *Selected Values of Hydrocarbons and Related Compounds* (Rossini, 1952; C.C. Williams, 1975). Thermodynamic properties of explosives are listed by Kinney (1962) and Kinney and Graham (1985).

Thermodynamic properties may also be estimated by theoretical methods, which are generally based on group contributions. A number of methods are described by Reid and Sherwood (1958, 1966), Reid, Prausnitz and Sherwood (1977) and Reid, Prausnitz and Poling (1987).

Thermodynamic properties of selected substances are given in Table 17.8.

17.4.2 Gas expansion energy

Explosions can also be caused by gas or liquid under high pressure. The energy released in an explosive expansion of a compressed gas is again given by Equation 17.4.1.

Considering an ideal gas, for 1 mol of the gas, the limiting value of the energy of explosion, assuming an ideal gas and isothermal expansion, is

$$W = \int_1^2 P \, \mathrm{d}V \approx T \, \Delta S = RT \ln(P_1/P_2) \qquad [17.4.23]$$

where the subscript 1 denotes the initial state and 2 the final state.

Assuming isentropic expansion, the limiting value of the energy of explosion is

$$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1} \qquad [17.4.24]$$

or eliminating V_2 using $PV^{\gamma} = \text{constant}$

$$W = \frac{P_1V_1}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{(1-\gamma)/\gamma}\right] \qquad [17.4.25]$$

where γ is the ratio of the gas specific heats.

17.4.3 Liquid expansion energy

The energy released in an explosive expansion of a liquid is

$$U_1 = \frac{1}{2}\beta P^2 V \qquad [17.4.26]$$

where U_1 is the liquid strain energy, V is the volume of the vessel and β is the bulk modulus of the liquid.

17.4.4 Vessel metal strain energy

The elastic strain energy in a cylindrical vessel neglecting the ends is given by Manning and Labrow (1971) as

$$U_{\text{m}} = \frac{P^2V}{2E}\left[\frac{3(1-2\nu) + 2K^2(1+\nu)}{K^2 - 1}\right] \qquad [17.4.27]$$

where E is Young's modulus, K is the diameter ratio, U_{m} is the metal strain energy and ν is Poisson's ratio. The

Table 17.8 *Thermodynamic properties of selected substances*

	State	ΔE_f^o (kcal/mol)	ΔH_f^o (kcal/mol)	ΔA_f^o (kcal/mol)	ΔF_f^o (kcal/mol)	S^o (cal/mol K)	$\Delta H_c^{o(a)}$ (kcal/mol)
C (graphite)	s	0	0	0	0	1.3609	−94.052
CO	g	−26.722	−26.416	−33.104	−32.808	47.301	−67.636
CO_2	g	−94.052	−94.052	−94.260	−94.260	51.061	–
H_2	g	0	0	0	0	31.211	−68.317
H_2O	g	−57.502	−57.798	−56.339	−54.636	45.106	–
N_2	g	0	0	0	0	45.767	–
O_2	g	0	0	0	0	49.003	–
Cl_2	g	0	0	0	0	53.286	–
Acetylene	g		54.194		50.000	47.997	−310.615
Benzene	g		19.820		30.989	64.34	−789.08
n-Butane	g		−30.15		−4.10	74.12	−687.982
Cyclohexane	g		−29.43		7.59	71.28	−936.88[b]
Ethane	g		−20.236		−7.860	54.85	−372.820
Ethylene	g		12.496		16.282	52.45	−337.234
Methane	g		−17.889		−12.140	44.50	−212.798
Propane	g		−24.820		−5.614	64.51	−530.605
Propylene	g		4.879		14.990	63.80	−491.987
Styrene	g		35.22		51.10	82.48	–
Toluene	g		11.950		29.228	76.42	−943.58
TNT	s	−13.0				65	

[a] Final products CO_2(g), H_2O(l).
[b] Heat of combustion value is for liquid.
Notes: (1) g, gas; l, liquid; s, solid.
Sources: First eight items and last item. All properties except ΔH_c^o: Kinney (1962). Other items. ΔH_f^o, ΔF_f^o, S^o: C.C. Williams (1975). All items. ΔH_c^o: Washburn (1926); Rossini (1952); Perry (1950) (quoted by Hougen, Watson and Ragatz, 1954–).

elastic strain energy of the metal is usually small compared with the chemical and fluid expansion energies.

17.4.5 Vessel burst energy: ideal gas

For the energy of explosion in the bursting of a vessel containing fluid under pressure, it is necessary to distinguish between cases where the fluid can be treated as an ideal gas and those where it cannot.

Taking the ideal gas case first, there are a number of treatments available. Accounts include those of Brode (1955, 1959), Kinney (1962), W.E. Baker (1973), Adamczyk (1976), Strehlow and Ricker (1976), W.E. Baker *et al.* (1983) and the CCPS (1994/15).

The literature reveals a variety of approaches based on different treatments of the thermodynamics. The two most widely used relations appear to be those of Brode (1959) and of W.E. Baker (1973).

In the treatment given by Brode (1959) the energy of explosion is the energy required to raise the pressure of the gas at constant volume from atmospheric pressure to the initial, or burst, pressure. It is thus the difference in the internal energies of the gas at the initial and final pressures. The internal energy is

$$E = \frac{PV}{\gamma - 1} \qquad [17.4.28]$$

where E is the internal energy, P is the absolute pressure in the vessel and V is the volume of the vessel. Brode's equation is

$$E_{Br} = \frac{(P_1 - P_o)V}{\gamma_1 - 1} \qquad [17.4.29]$$

where E_{Br} is Brode's energy of explosion, P is the absolute pressure, V is the volume of the vessel and the subscripts 1 and o denote 'initial vessel' and 'atmospheric', respectively.

The treatment of W.E. Baker (1973) is based on the work done on the surroundings in an isentropic expansion. Baker's equation is

$$E_{Ba} = \frac{P_1V_1 - P_oV_2}{\gamma_1 - 1} \qquad [17.4.30]$$

where E_{Ba} is Baker's energy of explosion and the subscripts 1 and 2 denote the initial and final conditions. For an isentropic expansion (PV^γ = constant), Equation 17.4.30 can be written as

$$E_{Ba} = \frac{P_1V_1}{\gamma_1 - 1}\left[1 - \left(\frac{P_o}{P_1}\right)^{(\gamma-1)/\gamma}\right] \qquad [17.4.31]$$

A third relation for the energy of explosion is that given by Kinney (1962). This is based on work done in isothermal expansion and is

$$E_{Ki} = nRT \ln(P_1/P_o) \qquad [17.4.32]$$

where E_{Ki} is Kinney's energy of explosion and n is the number of moles.

Other expressions for the energy of explosion include those of Adamczyk (1976) and Aslanov and Golinsky (1989).

Aslanov and Golinsky (1989) extend Baker's approach to take into account the internal energy of the air displaced by the expanding gas. Their expression, which contains an additional term to allow for this effect, is

$$E_{AG} = \frac{P_1V_1 - P_oV_2}{\gamma_1 - 1} + \frac{P_o(V_2 - V_1)}{\gamma_o - 1} \qquad [17.4.33]$$

where E_{AG} is the Aslanov–Golinsky energy of explosion.

Comparisons of the expressions for energy of explosion have been given by Strehlow and Ricker (1976) and the CCPS (1994/15). The former define a scaling radius

$$R_o = \left(\frac{E}{P_o}\right)^{\frac{1}{3}} \qquad [17.4.34]$$

where R_o is the scaling radius (m).

They then compare the results given by the equations for the energy of explosion of Brode, Baker and Kinney at a given actual distance r_o and dimensionless distance R_o/r_o as shown in Figure 17.6(a). At higher pressure ratios the results given by the Kinney equation diverge from those given by the other equations. They recommend the use of the Brode equation.

The CCPS (1994/15) give plots of the ratio of the energies of explosion given by Baker, by Adamczyk and by Aslanov and Golinksy workers to that given by Brode. This comparison indicates that the values yielded by the other expressions tend to those of the Brode equation at higher pressures, but there is a considerable divergence at lower pressures. For the latter they state that the ratio of values obtained from the different models is as high as four. In the method given for vessel bursts the CCPS use the Brode equation.

The preferred method for the estimation of the explosion energy of gas-filled vessels appears to be that of Brode. The main alternative is that of Baker. The method of Kinney considerably overestimates the explosion energy.

The following version of the Brode equation in terms of TNT equivalence has been given in the Second *Canvey Report* (HSE, 1981a):

$$E = 1.43 \times 10^{-6} \frac{(P_1 - P_o)V}{\gamma^{-1}} \qquad [17.4.35]$$

where E is the explosion energy (te of TNT), P_1 the initial pressure in the vessel (kPa), P_o is the pressure of the surroundings (kPa) and V is the volume of the vessel (m^3).

As an illustration, consider the energy of explosion of 1 kmol of air at 100 bar and 20°C. The volume V of the gas is

$$V = nRT/P$$

$$= 10^3 \times 8.314 \times 293/(100 \times 10^5)$$

$$= 0.243\ m^3$$

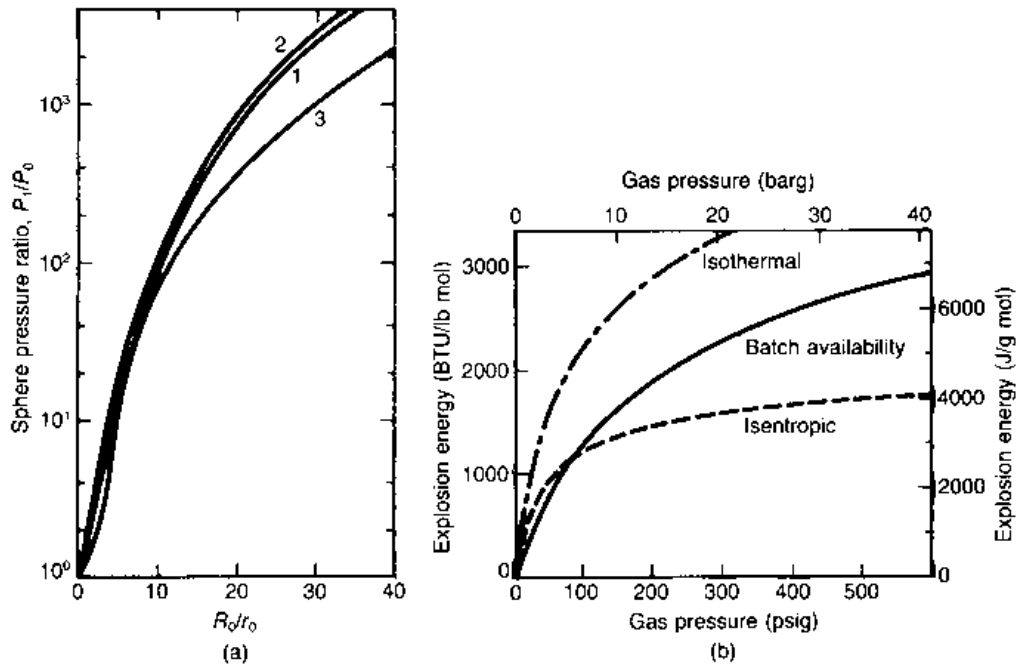

Figure 17.6 *Energy of explosion in a vessel burst. (a) Comparison by Strehlow and Ricker (1976): curve 1, model of Brode (1955); curve 2, model of W.E. Baker (1953); and curve 3, model of Kinney (1962) (Courtesy of the American Institute of Chemical Engineers). (b) Comparison by Crowl (1992a) (Courtesy of Butterworth-Heinemann)*

Using the Brode Equation 17.4.29, the explosion energy E_{ex} is

$$E_{ex} = [(100-1) \times 10^5 \times 0.243]/(1.4-1)$$

$$= 0.6 \times 10^7 \text{ J}$$

$$= 6 \times 10^3 \text{ kJ}$$

$$= 1.43 \times 10^6 \text{ cal}$$

The energy in this explosion is thus equivalent to the following quantity of TNT:

$$= \frac{1.43 \times 10^6}{1120}$$

$$= 1280 \text{ g of TNT}$$

$$= 1.3 \text{ kg of TNT}$$

The distribution of this energy is discussed below.

17.4.6 Vessel burst energy: non-ideal gas, vapour, flashing liquid

For the energy of explosion in the bursting of a vessel containing fluid under pressure which is not an ideal gas but a non-ideal gas, vapour or flashing liquid, the foregoing approach is not suitable.

In this case the energy of explosion is obtained as the difference in the internal energy between the initial and final states assuming an isentropic expansion, using suitable thermodynamic diagrams or tables.

Since it is the specific internal energy e which is of interest and since thermodynamic data tend to be given in terms of specific enthalpy, use may be made of the relation

$$h = e + pv \qquad [17.4.36]$$

where e is the specific internal energy, h is the specific enthalpy, p is the absolute pressure and v is the specific volume.

The initial condition of the fluid is defined in terms of the variables p_1, v_1, s_1 and h_1 and the final condition in terms of the variables p_2, v_2, s_2 and h_2, where s is the specific entropy and the subscripts 1 and 2 denote the initial and final states. An isentropic expansion is performed from p_2 to p_1, where the latter equals atmospheric pressure p_o, so that

$$s_2 = s_1 \qquad [17.4.37]$$

The enthalpy change $(h_1 - h_2)$ is obtained, and from this the internal energy change $(e_1 - e_2)$ using Equation 17.4.36. Then

$$E_{ex} = n(e_1 - e_2) \qquad [17.4.38]$$

where E_{ex} is the energy of explosion and n the number of moles.

For expansion of a vapour there are several different cases which may arise. The fluid may be (1) a vapour superheated in both states, (2) a vapour wet in both states or (3) a vapour superheated in state 1 but wet in state 2.

The wetness of the vapour may be expressed as

$$x = \frac{\phi - \phi_f}{\phi_g - \phi_f} \qquad [17.4.39]$$

where x is the wetness of the vapour and ϕ is a variable, and the subscripts f and g denote saturated liquid and saturated vapour, respectively. In this equation the variable ϕ may be replaced by v, s, e or h.

The following equation given by the CCPS is useful in interpolating in thermodynamic tables:

$$e_2 = (1-x)h_f + xh_g - (1-x)p_o v_f - xp_o v_g \qquad [17.4.40]$$

The CCPS gives data on the work of expansion for a limited set of fluids, namely ammonia, carbon dioxide, ethane, isobutane, nitrogen, oxygen and propane.

17.4.7 Energy distribution in an explosion

The energy distribution in an explosion is shown schematically in Figure 17.7. Only a fraction of the total energy in the explosion appears in the blast wave or the missiles. Some is dissipated as heat radiation. Other energy appears as potential energy, essentially thermal energy, in the explosion products and eventually, as they lose kinetic energy, in the fragments.

17.4.8 Energy distribution in a vessel burst explosion

For vessel rupture the effects of an explosion with a given energy release depend on the way in which the energy is distributed.

The total energy E_s in a system is the sum of the chemical energy E_1, the fluid expansion energy E_2 and the vessel strain energy E_3:

$$E_s = E_1 + E_2 + E_3 \qquad [17.4.41]$$

For a catastrophic or near-catastrophic failure of a vessel the *High Pressure Safety Code* gives the energy distribution shown in Table 17.9. The energy in the shock, or blast, wave is given for this case as between 40% and 80% of the explosion energy. A value of 50% is often used. The energy in the fragments is given for the case considered as between 20% and 80%.

The explosion energy in vessel rupture and its partition between blast and missiles is discussed further Section 17.27. The energy imparted to missiles in also considered in Section 17.34.

17.4.9 Energy of a vapour cloud explosion: yield factor

In a vapour cloud explosion the energy in the blast wave is generally only a small fraction of the energy theoretically available from the combustion of all the material in the cloud. The ratio of the actual energy in the explosion to that theoretically available is variously termed the 'explosion efficiency', 'yield factor' or simply 'yield'.

This ratio is referred to here as the yield factor, or yield, and has a value less than unity. It is to be distinguished from the yield ratio, described in the next subsection.

If it is assumed that all the flammable material in the cloud is available for combustion, the combustion energy theoretically available is the product of the total mass of flammable material and of the heat of combustion. On this basis, explosion efficiencies are typically 1–10%.

In some accounts, however, only the part of the cloud which is within the flammable range is considered. Often

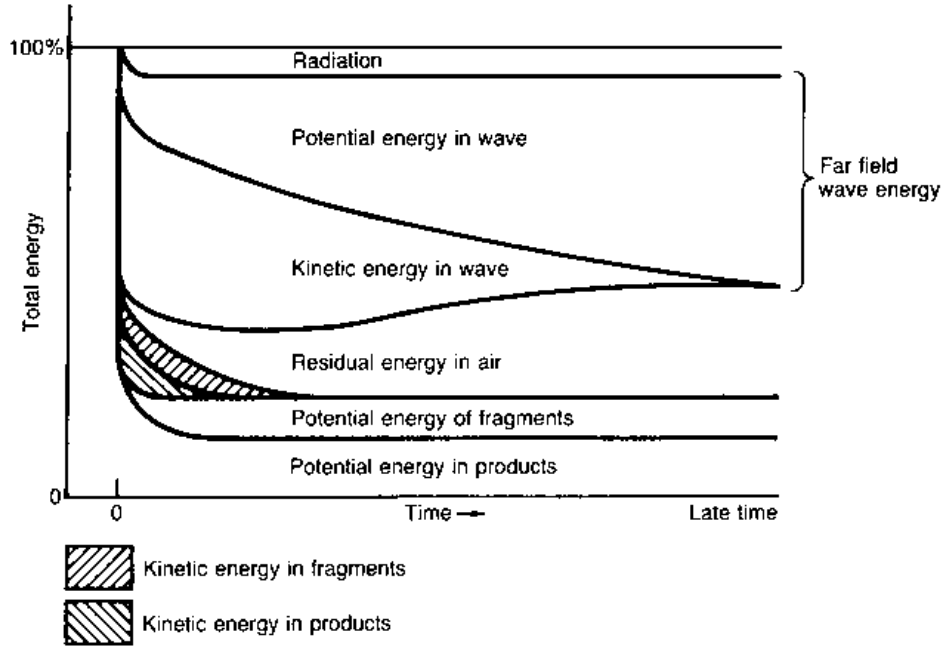

Figure 17.7 *Schematic energy distribution in a chemical explosion (after Strehlow and Baker, 1976; Stull, 1977)*

Table 17.9 *Approximate distribution energy of explosion of a bursting vessel (after B.G. Cox and Saville, 1975)*

	Shock wave energy	*Fragment kinetic energy*
Complete shattering of vessel due to brittle failure	$0.8E_s$	$0.2E_s$
Ejection of a major vessel section such as an end closure of a short, large bore vessel	$0.4E_s$	$0.6E_s$

this is up to an order of magnitude less than the total cloud. Consequently, explosion efficiencies calculated on this basis tend to be as much as an order of magnitude greater than those based on combustion of the whole cloud.

The energy of vapour cloud explosions is discussed further in Section 17.28.

17.4.10 Blast energy of ground level explosion: yield ratio

A large proportion of explosions of interest in process plants occur at ground level. For such an explosion the ground forms a barrier to the explosion. For an explosion at ground level the blast wave has a strength that corresponds to an apparent energy of explosion which exceeds that for a free-air explosion by a yield ratio lying between one and two. In other words, for a ground level explosion the apparent energy to be used in the correlations for the blast wave parameters is multiplied by the yield ratio, typically two.

In general, the yield ratio is determined by two factors. These are:

(1) explosion symmetry;
(2) crater formation.

A free-air explosion has spherical symmetry, whilst a ground level explosion has hemispherical symmetry. On the basis of symmetry alone, the apparent energy in the blast wave from a ground level explosion will be twice that in the blast wave from a free air explosion. In other words, the yield ratio of the ground level explosion will be two.

If, however, energy is expended in crater formation the yield ratio will be less. This is the case with explosions of condensed phase explosives. Thus, for example, yield ratios for TNT explosions at or near ground level frequently lie in the range 1.5–2. A typical value of the yield ratio for explosives is 1.8.

On the other hand, vapour cloud explosions tend not to give a crater. There was no crater formed, for example, at Flixborough. Thus, for a vapour cloud explosion at ground level the yield ratio approaches two.

As already described, the effective energy release in a vapour cloud explosion is only a small fraction of the total energy theoretically available and the ratio of these

two energies is expressed as an explosion efficiency. If an explosion efficiency is utilized, it should be used in conjunction with the same yield ratio as was used in its original derivation. Frequently this yield ratio is not stated, but it appears in many cases to be unity.

For an explosion such as the bursting of a pressure vessel due to high gas pressure at ground level the explosion energy absorbed by the ground is again generally smaller than for a condensed phase explosion. Again the value of the yield ratio lies nearer to two.

It is not always clear what assumption should be made concerning the yield ratio, and it may be necessary to exercise judgement. For the calculation of the maximum peak overpressure from an explosion the conservative assumption is a yield ratio of two.

The term 'yield ratio' is used in work on condensed phase explosives (e.g. Kinney and Graham, 1985) and is therefore retained here, despite its similarity to the yield factor described in the previous subsection. The yield ratio has a value greater than unity. However, where only symmetry and not cratering is in question, use is also made here of the alternative term 'symmetry factor'. This is identical to the yield ratio if cratering is disregarded and has a value greater than unity.

It should be made clear that these considerations relate solely to the method of estimating the energy imparted to the blast wave. The actual energy of explosion remains the same whether the explosion is in free air or at ground level. In particular, the energy imparted to fragments is unaffected.

In some cases, equations for energy of explosion are quoted with a factor of two already incorporated. These equations are solely for use in estimating the blast wave parameters.

17.4.11 Energy of explosion from thermodynamic availability

As the texts indicate, the energy of explosion obtained from the Helmholtz free energy change is an approximation. Its use has been criticized by Crowl (1991) on the grounds that it applies to a constant temperature process, whereas in a real explosion the initial state of the substance may be at some higher temperature and/or pressure.

Accounts of the concept of availability are given by Keenan (1941) and Vogler and Weissman (1988). It has been applied by Crowl to the energy of explosion in general and in particular to explosions associated with combustion of gases (Crowl, 1991, 1992a) and with vessel bursts (Crowl, 1992a,c).

The thermodynamic background to the method is fully described by Crowl (1992a). The treatment here is confined to its application to the estimation of the energy of explosion for the cases of a vessel burst explosion and a chemical explosion.

For a vessel burst the explosion energy is the change in batch availability. Assuming ideal gas behaviour,

$$\Delta B = -R\left[T_a \ln\left(\frac{P_1}{P_a}\right) - T_1\left(1 - \frac{P_a}{P_1}\right)\right] - C_p\left[T_a \ln\left(\frac{T_2}{T_1}\right) - (T_2 - T_1)\right] \qquad [17.4.42]$$

where ΔB is the change in batch availability (kcal/mol), C_p is the specific heat at constant pressure (kcal/mol K), P is the absolute pressure (Pa), R is the universal gas constant (kcal/mol K), T is the absolute temperature (K), and the subscripts a, 1 and 2 denote ambient, initial state and final state, respectively.

For the case where the initial and final temperatures are equal to the ambient temperature ($T_1 = T_2 = T_a$), Equation 17.4.42 reduces to

$$\Delta B = -RT_a\left[\ln\left(\frac{P_1}{P_a}\right) - \left(1 - \frac{P_a}{P_1}\right)\right] \qquad [17.4.43]$$

Crowl discusses the various approaches to the estimation of the energy of explosion in a vessel burst, comparing values obtained from the isentropic and isothermal expansion treatments of Baker and of Kinney, given above as Equations 17.4.31 and 17.4.32, with his own method, as shown in Figure 17.6(b). The graph indicates that compared with the thermodynamic availability method the isentropic expansion method generally underestimates the energy of explosion, whilst the isothermal expansion method always overestimates it. In an isentropic expansion the final temperature is in fact not the ambient temperature but a much lower temperature. He advises against the use of the isentropic expansion method for the determination of the energy of explosion in vessel bursts.

As an illustration, consider the case given by Crowl. This is the determination of the energy of explosion of a cylinder containing 45.4 kg of nitrogen at 1.53×10^4 kPa at 298 K with an ambient pressure of 100 kPa. The mass of gas is thus 1.621 kg mol (45.5/28). Then, from Equation 17.4.43

$$\Delta B = -2.39 \text{ kcal/mol}$$

$$= -1621 \times 2.39$$

$$= -3870 \text{ kcal}$$

For a chemical explosion the explosion energy is the change in batch availability. For the energy change where the initial conditions of a gas/air mixture are ambient temperature and pressure,

$$\Delta B = (B)_{pr} - (B)_r \qquad [17.4.44]$$

where

$$B = \sum_{i=1}^{m} n_i(\phi_{oi} + RT_a \ln x_i) \qquad [17.4.45]$$

where B is the batch availability (kcal/mol), n_i is the number of moles of species i, m is the number of species, x_i is the mole fraction of species i, ϕ_o is the standard batch availability (kcal/mol) and subscripts pr and r denote the products and reactants, respectively.

If the gas/air mixture is at a pressure other than ambient, the batch availability of the reactants is adjusted by the addition of the term

$$\delta B = nRT_a\left[\ln\left(\frac{P_1}{P_a}\right) - \left(1 - \frac{P_a}{P_1}\right)\right] \qquad [17.4.46]$$

For the special case of explosion of a substance in stoichiometric combustion in pure oxygen at standard temperature and pressure the energy of explosion is simply the batch availability ϕ_o of the substance.

Two cases of chemical explosion given by Crowl are considered by way of illustration. The first is the calculation of the energy of explosion for the stoichiometric combustion of methane in air:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O\ (g)$$

The energy of explosion is obtained from Equation 17.4.44 using Equation 17.4.45 for the batch availability B. Considering 1 mol of methane:

Initial state

Species	*Moles,* n_i	*Mole fraction,* x_i	*Standard availability*		*Batch availability,*
			ϕ_{oi} (cal/mol)	$RT_a \ln x_i$ (cal/mol)	B (cal/mol)
CH_4	1.00	0.0951	195 500	−1 393	194 107
O_2	2.00	0.1901	0	−983	−1 966
N_2	7.52	0.7148	0	−199	−1 496
Total	10.52				190 645

and

Final state

Species	*Moles,* n_i	*Mole fraction,* x_i	*Standard availability*		*Batch availability,*
			ϕ_{oi} (cal/mol)	$RT_a \ln x_i$ (cal/mol)	B (cal/mol)
CO_2	1.00	0.0951	0	−1 393	−1 393
H_2O	2.00	0.1901	2 054	−983	2 142
N_2	7.52	0.7148	0	−199	−1 496
Total	10.52				− 747

Then

$$\Delta B = (-747) - (190\,645)$$

$$= -191\,392 \text{ cal/mol of methane}$$

The second case is the energy of explosion of a mixture of 85% methane and 15% oxygen initially at 10 atm and 298 K. The stoichiometry for the combustion products is as follows: CH_4 77.5%, O_2 0%, CO_2 7.5% and H_2O 15%. Proceeding as before and considering 1 mol of mixture:

Initial state

Species	*Moles,* n_i	*Mole fraction,* x_i	*Standard availability*		*Batch availability,*
			ϕ_{oi} (cal/mol)	$RT_a \ln x_i$ (cal/mol)	B (cal/mol)
CH_4	0.85	0.85	195 500	−96.2	166 096
O_2	0.15	0.15	0	−1 123	−168
Total	1.00				165 925

and

Final state

Species	*Moles,* n_i	*Mole fraction,* x_i	*Standard availability*		*Batch availability,*
			ϕ_{oi} (cal/mol)	$RT_a \ln x_i$ (cal/mol)	B (cal/mol)
CH_4	0.775	0.775	195 500	150.7	151 396
O_2	0	0	0		
CO_2	0.075	0.075	0	−1 535	−115
H_2	0.15	0.15	2 054	−1 123	−140
Total	1.000				151 141

Further, from Equation 17.4.46

$$\delta B = 830 \text{ cal}$$

Then

$$\Delta B = (151\,141) - (165\,925 + 830)$$

$$= -15\,614 \text{ cal/mol of mixture}$$

Crowl states that the energy of explosion computed using the thermodynamic availability method is always less than that obtained from the heat of combustion method. For stoichiometric mixtures the difference is of the order of 5–10%, but for other conditions such as non-stoichiometric mixtures and higher initial pressure and temperature the difference can be substantial.

The application of the method requires the use of data on the standard availability, which is not one of the thermodynamic quantities normally listed. Crowl (1992a) provides a table of standard availabilities for a quite large number of substances.

The following values are given for the standard availability of some common gases at standard conditions (1 atm, 298 K) and final state (H_2O (l)):

Substance	*Standard availability,* ϕ_o (kcal/mol)
Methane	195.5
Ethane	350.73
Propane	503.93
n-Butane	656.74
Ethylene	318.18
Propylene	467.81
Acetylene	295.21
Hydrogen	56.69
O_2 (g)	0
CO_2 (g)	0
H_2O (l)	0

17.5 Deflagration inside Plant

The explosion of a flammable mixture in a process vessel or pipework may be a deflagration or a detonation. These two types of explosion differ fundamentally and require different countermeasures. Both types, but particularly detonation, can be very destructive.

The conditions for a deflagration to occur are that the gas mixture is within the flammable range and that there is a source of ignition of that the mixture is heated to its autoignition temperature.

The conditions for a detonation to occur are similar except that in this case the mixture should be within the detonable range. If the source of ignition is sufficiently strong, detonation may be initiated directly. Alternatively, a deflagration may undergo transition to a detonation. This transition occurs in pipelines but is most unlikely to occur in vessels.

17.5.1 Sources of ignition

The sources of ignition usually considered are those outside the process plant, but ignition sources can occur inside vessels and pipework also. These include:

(1) flames and hot surfaces;
(2) sparks;
(3) chemicals –
  (a) unstable compounds,
  (b) reactive compounds and catalysts,
  (c) pyrophoric iron sulphide;
(4) static electricity;
(5) compression.

This list is sufficient to show that there is no shortage of possible ignition sources inside the plant.

The wide variety of conditions which can cause ignition is illustrated by the fact that compressed air at 60 psig striking a suitably shaped depression in the end of a piece of wood can ignite the latter (W.G. High, 1976).

If a flammable mixture may be present, precautions should be taken to eliminate all ignition sources. But it is prudent to assume that, despite these efforts, a source of ignition will at some time occur.

Ignition can also occur if the flammable mixture is heated to its autoignition temperature.

17.5.2 Deflagration in vessels

For a deflagration at constant volume in a sphere the maximum explosion pressure is

$$\frac{P_2}{P_1} = E \qquad [17.5.1]$$

with

$$E = \frac{n_2 T_2}{n_1 T_1} \qquad [17.5.2a]$$

$$= \frac{M_1 T_2}{M_2 T_1} \qquad [17.5.2b]$$

where E is the expansion ratio, M is the molecular weight of the gas mixture, n is the number of moles in the gas mixture, P is the absolute pressure, T is the absolute temperature, and the subscripts 1 and 2 denote the initial and final states, respectively.

For deflagration of hydrocarbons the ratio of the maximum explosion pressure to the initial pressure has been quoted as being approximately 8 for hydrocarbon–air mixtures and 16 for hydrocarbon–oxygen mixtures (Zabetakis, 1965 BM Bull. 627; W.G. High, 1976). These values apply for initial pressures in the range 1–40 bar, for initial temperatures in the range 0–300°C and for relatively small volumes of a few cubic metres.

However, as described in Section 17.7, the values quoted for the final pressure attained in deflagration in a closed vessel are often underestimated due to the use of constant pressure rather than constant volume assumptions. On the correct basis of constant volume combustion, for hydrocarbon–air mixtures the ratio of the maximum explosion pressure to the initial pressure is approximately as follows:

$$\frac{P_2}{P_1} \approx 10 \qquad [17.5.3]$$

This is the order of pressure rise in deflagrative combustion, for example, in the results given in Table 17.7.

For conventionally designed pressure vessels the bursting pressure P_b is of the order of

$$\frac{P_b}{P_1} \approx 4 - 5 \qquad [17.5.4]$$

Hence in the absence of explosion relief the deflagration of a hydrocarbon–air mixture is easily capable of bursting a pressure vessel.

If the explosion relief is to be effective, it must act within a period which is generally much less than 1 second. Methods of explosion relief are available which do this and are discussed in Section 17.12.

17.5.3 Pressure piling

If an explosion occurs in a compartmented system in which there are separate but interconnected spaces, a situation can arise in which the pressure developed by the explosion in one space causes a pressure rise in the unburnt gas in an interconnected space, so that the enhanced pressure in the latter becomes the starting pressure for a further explosion. This effect is known as pressure piling, or cascading.

The type of system geometry in which pressure piling is liable to occur is illustrated in Figure 17.8(a). If the initial explosion occurs in space A, this may cause pressure piling in space B. If the final pressure in A is x times the initial pressure, a simplified argument would suggest that the final pressure in B might in the worst conceivable case be x^2 times the initial pressure in both spaces.

An account of pressure piling has been given by Fitt (1981a,b). The phenomenon of pressure piling was first detected by Beyling (1906) in work on flameproof

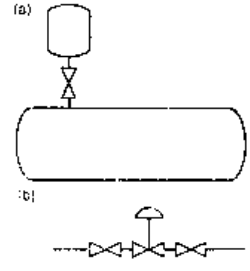

Figure 17.8 *Plant configuration to illustrate pressure piling: (a) compartmented tube system; (b) linked tube system*

Table 17.10 *Some experiments on pressure piling (after Fitt, 1981a)*

Worker(s)	*Apparatus*	*Compartment volume ratio*
Beyling (1906)	Compartmented pipe	2
Beyling (1906)	Link tube	11.7
Grice and Wheeler (1929)	Link tube	12 and 16.7
Coward and Wheeler (1934)	Compartmented pipe	Many compartments
Gleim and March (BM 1952 RI 4908)	Compartmented pipe	1.0–7.0
T.A.J. Brown (1959)	Link tube	13.5
J. Singh (1977)	Link tube	5.0–32.0
Bartknecht (1981a)	Link tube	5.0

Worker(s)	*Larger compartment diameter or side* (cm)	*Connecting passage diameter* (cm)	*Maximum observed peak pressure enhancement ratio*
Beyling (1906)	33.5	3.0	1.3
Beyling (1906)	33.5	2.0	2.3
Grice and Wheeler (1929)	45.8[a] and 50	2.5	2.0
Coward and Wheeler (1934)	30.6	2.5	Not studied[b]
Gleim and March (BM 1952 RI 4908)	30.6[a]	5.1–25.4	4.0
T.A.J. Brown (1959)	15.2	0.6–2.5	4.0
J. Singh (1977)	30.5	1.3–5.1	3.7
Bartknecht (1981a)			3.1

[a] Square section.
[b] Flame front projection.

electrical equipment and has subsequently been studied by a number of workers. Table 17.10 lists some of the experimental work done on pressure piling.

Fitt distinguishes between studies done on compartmented tube systems and linked tube systems, as shown in Figures 17.8(a) and 17.8(b), respectively. He also points out that there are two separate effects, which he calls flame front projection (FFP) and peak pressure enhancement (PPE). The first causes a very rapid rise of pressure, the second an enhanced final pressure.

Fitt states that in compartmented systems, pressure piling is observed with low compartment volume ratios and high connecting orifice-to-enclosure diameter ratios, whereas in link tube systems a volume ratio of at least 5:1 appears to be required for peak pressure enhancement. He suggests that there is a mechanism of pressure piling in compartmented systems which is suppressed in link tube systems.

The enhancement of pressure is limited by the fact that the total pressure volume energy cannot exceed that which would arise in an uncompartmented enclosure. If pressure piling occurs in one space, the maximum pressure in the remaining space must be reduced. At some stage the pressure differential will cause back venting, which lowers the peak value.

For hydrocarbon–air mixtures the maximum pressure obtained in combustion is about eight times the initial pressure. Thus, taking a peak pressure enhancement factor of 4, the maximum pressure obtained with pressure piling would be of the order of 30. Pressure piling can therefore give a very large increase in the maximum pressure rise in the plant.

With regard to design to avoid pressure piling, Fitt states that in link tube systems the peak pressure enhancement is unlikely to exceed a factor of 4. This is the maximum enhancement obtained in the experiments given in Table 17.10. The peak pressure enhancement in compartmented tube systems is less predictable, and such systems should be avoided. Pressure piling may be significant not only in the main process plant but in other equipment also. As already mentioned, much of the work on pressure piling has been concerned with flameproof equipment. This aspect is considered further in Chapter 16.

17.5.4 Deflagration in pipes

Whereas in a vessel deflagration results in a pressure rise which is uniform throughout the vessel, this is not so in a pipe, where the explosion velocity and explosion pressure can change along the length of the pipe.

An account of deflagration in pipes has been given by Bartknecht (1981a). He defines three cases:

Case 1: Pipe open at one end, ignition at open end

Case 2: Pipe open at one end, ignition at closed end

Case 3: Pipe closed at both ends.

In order to understand the phenomena involved, it is necessary to consider all three cases.

The explosion velocity is given by the relation

$$v_{ex} = \phi v_n + v_d \qquad [17.5.5]$$

where v_d is the displacement velocity, v_{ex} is the explosion velocity, v_n the normal burning velocity and ϕ the ratio of the area of the flame front to the cross-sectional area of the pipe. The displacement velocity v_d is the velocity of the unburned mixture, and the explosion velocity is the visible flame velocity. The equation applies to all three cases, but for that of an open pipe with ignition at the open end the displacement velocity is zero.

For the open pipe with ignition at the open end (case 1), the displacement velocity is zero, but for ignition at the closed end (case 2) it is high, being some 80–90% of the explosion velocity. In this latter case only part of the gas mixture, theoretically 1/7, is burned within the pipe, the rest being ejected from the open end and burned outside. The high displacement velocity also results in much higher turbulence, a higher flame front area, and a higher value of ϕ, in this latter case.

For an open pipe with ignition at the closed end with large diameter pipes ($\geq$400 mm) the explosion velocity exhibits an approximately linear increase along the length of the pipe. With smaller diameter pipes this continuous increase is no longer observed. As the pipe diameter is decreased, a critical diameter is reached at which the flame propagation no longer occurs.

For an open pipe with ignition at the closed end the explosion pressure P_{ex} increases linearly with the explosion velocity, as shown in line 1 of Figure 17.9(a). This effect is independent of pipe diameter.

Thus for the case of a 1600 mm diameter pipe 10 m long open at one end, Bartknecht quotes, for ignition at the open end, values of v_{ex} and P_{ex} of 4 m/s and 0.02 bar and, for ignition at the closed end, values of 150 m/s and 0.2 bar, respectively.

If the flow is highly turbulent and if the pipe is long enough, the explosion velocity can reach a value such that detonation, or quasi-detonation, occurs. The reference to quasi-detonation applies particularly to methane. It is difficult to cause methane to detonate, and although it exhibits detonation-like behaviour, the flame front and shock wave can separate, whereas in a normal detonation they are coupled.

Table 17.11 shows the pipe lengths required for run-up to detonation for the three gases methane, propane and hydrogen with flame jet ignition in pipes of 100, 200 and 400 mm diameter.

Turning to the case of a pipe closed at both ends (case 3), and considering first a quiescent gas mixture, experimental results given by Bartknecht show that the explosion velocity initially increases along the length of the pipe due to a high displacement velocity, but since the gas is confined, the displacement velocity and the explosion velocity then decrease. For gases such as methane and propane, the net effect is to cause the explosion velocity to pass through a maximum, and for the value of that maximum to be less than that attained in an open pipe with ignition at the closed end. There is in effect a braking action. Hydrogen constitutes an exception: the explosion velocity is the same in both configurations and does not pass through a maximum.

If the gas mixture is turbulent, however, there is no such braking action. In this case in a pipe closed at both ends all three gases will run up to detonation, or quasi-detonation. The distance required to do this is longer than for a pipe with one end open, but is less than 30 m.

For a pipe closed at both ends, the explosion pressure again increases linearly with the explosion velocity, but since all the gas is burned the explosion pressure is several bar higher than for the open pipe case, as shown in line 2 in Figure 17.9(a).

The pressures developed in detonation, or quasi-detonation, of the three gases mentioned in pipes of 100 and 200 mm diameter with flame jet ignition are shown in Table 17.12. There are several points worthy of note. The pressures tend to be higher in the small diameter pipe. The pressures on the end flange P_{pf} are some three times those on the pipe wall P_{pw}. And the pressures given by hydrogen are less than those given by the other two gases.

17.5.5 Plant design

The hazard of an explosion should in general be minimized by avoiding flammable gas–air mixtures inside plant. It is bad practice to rely solely on elimination of sources of ignition.

If the hazard of a deflagrative explosion may nevertheless exist, the possible design policies include (1) design for full explosion pressure, (2) use of explosion suppression or relief, and (3) the use of blast cubicles.

It is sometimes appropriate to design the plant to withstand the maximum pressure generated by the explosion. Often, however, this is not an attractive solution. Except for single vessels, the pressure piling effect creates the risk of rather higher maximum pressures. This approach is liable, therefore, to be expensive.

An alternative and more widely used method is to prevent overpressure of the containment by the use of explosion suppression or relief. This is discussed in more detail in Section 17.12.

Table 17.11 *Pipe lengths (m) for acceleration to detonation (after Bartknecht, 1981a)* (Courtesy of Springer-Verlag)

	Pipe diameter (mm)		
Gas	100	200	400
Methane	12.5	18.5	>30
Propane	12.5	17.5	22.5
Hydrogen	7.5	12.5	12.5

Table 17.12 *Some pressures (bar) in a pipeline closed at both ends following a detonation, or quasi-detonation (after Bartknecht, 1981a)* (Courtesy of Springer-Verlag)

	Pipe diameter 100 mm		*Pipe diameter 200 mm*	
Gas	P_{pw}	P_{pf}	P_{pw}	P_{pf}
Methane	35	100	25	80
Propane	35	95	25	75
Hydrogen	23	56	23	40

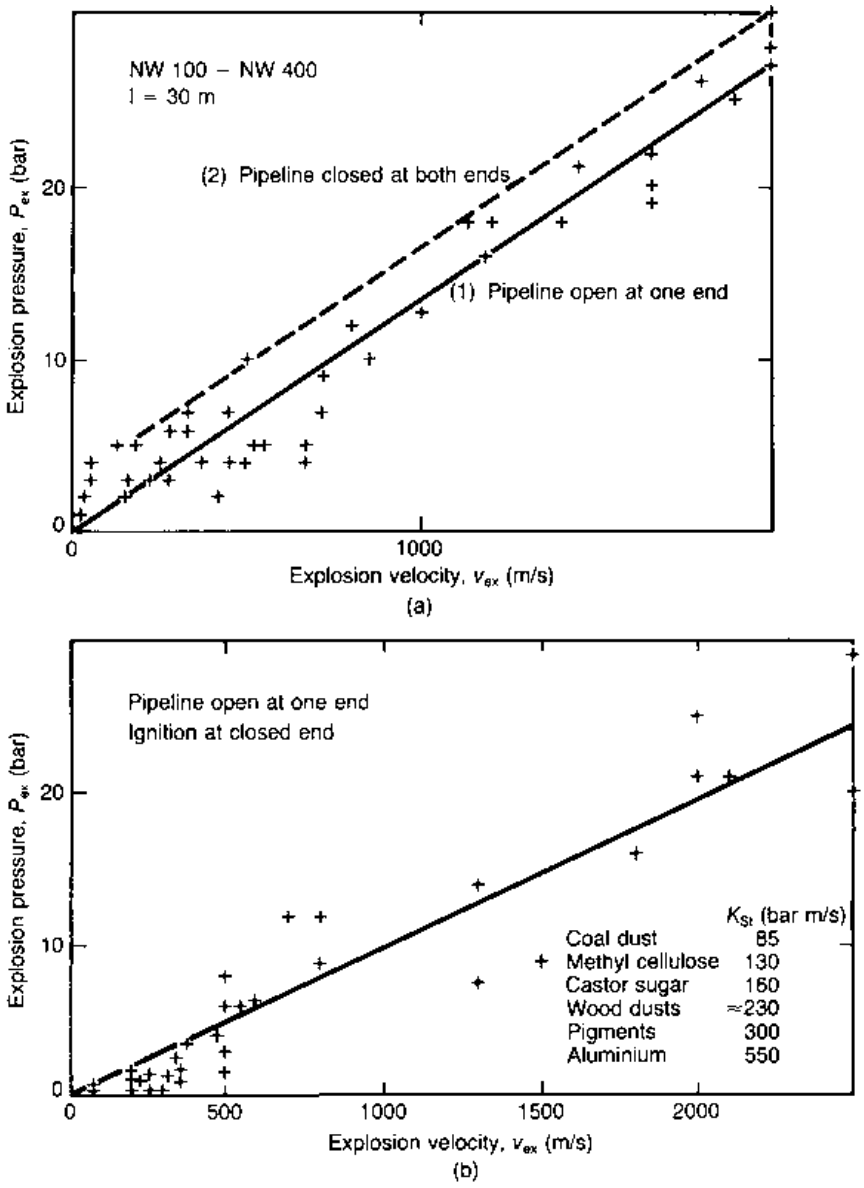

Figure 17.9 *Explosion pressure in pipes (after Bartknecht, 1981a). (a) Flammable gas: line 1, flammable gas in a pipe of diameter 100–400 mm and length 30 m open at one end; line 2, flammable gas in a pipe of the same dimensions closed at both ends. (b) Flammable dusts: dusts with K_{st} values of 85–550 bar m/s in a pipe of diameter 400 mm and length 40 m open at one end with ignition at the closed end (Courtesy of Elsevier Science)*

In some cases the plant may be enclosed within a blast resistant cubicle. Total enclosure is normally practical for energy releases up to about 5 kg TNT equivalent. For greater energy releases a vented cubicle may be used, but tends to require an appreciable area of ground to avoid blast wave and missile effects.

It is more difficult to design for a detonative explosion. A detonation generates much higher explosion pressures. Explosion suppression and relief methods are not normally effective against a detonation. Usually the only safe policy is to seek to avoid this type of explosion.

Direct initiation of detonation in ordinary flammable gas–air mixtures is generally improbable. Avoidance of detonation depends mainly, therefore, on elimination of conditions under which transition from deflagration to detonation can occur in equipment such as pipelines.

Where a significant explosion hazard exists, the possible consequences of explosion should be reviewed.

17.6 Detonation inside Plant

Detonation of a flammable gas–air mixture may occur by direct initiation of detonation by a powerful ignition source or by transition from deflagration.

The transition from deflagration to detonation requires a strong acceleration of the flame front. It occurs in pipelines but is very improbable in vessels. The transition from deflagration to detonation is a complex process. The properties of the detonation, however, are fairly well defined and depend essentially on the properties and condition of the unburnt gas.

17.6.1 Detonation in vessels

A general account of the pressures which may be generated by detonation inside plant has been given in Section 17.2. In practical terms, the peak pressure P_2 resulting from a detonation of a hydrocarbon–air mixture in a containment such as a vessel initially at atmospheric pressure P_1 may be about 20 bar:

$$\frac{P_2}{P_1} \approx 20 \qquad [17.6.1]$$

This is the order of pressure rise, for example, in the results given in Table 17.7.

17.6.2 Detonation in pipes

The transition from deflagration to detonation was discussed in Sections 17.2 and 17.5, where information was given on the run-up length to detonation and on the pressures exerted both on the pipe wall and on the end flange.

Accounts of detonation in pipes have been given by a number of workers, including Craven and Greig (1967), Munday (1971b) and Bartknecht (1981a).

Craven and Greig describe experimental work on the pressure generated by the detonation of ammonia–nitrous oxide mixtures in 3 and 4 in. pipes initially at atmospheric pressure. Determinations were made of the incident pressure and of the reflected pressure. The latter was determined from the distortion suffered by test plates bolted to the end of the pipe. It was found that the velocity, the incident pressure and the reflected pressure all rose rapidly with distance from the ignition source to a peak value and then fell to a lower, plateau value. Thus the transition from deflagration to detonation was associated with high but unstable velocities and pressures. In the 3 in. pipe with a 50:50 ammonia–nitrous oxide mixture the incident pressure peak and plateau values were about 1250 and 370 $lb_f/in.^2$, and the reflected pressure peak and plateau values were about 4800 and 1100 $lb_f/in.^2$, respectively.

The effects of detonation in a pipe system vary. In some cases damage is confined to blank ends and sudden changes of direction. In other cases the pipe may be ripped open from end to end.

17.6.3 Pressure piling

The phenomenon of pressure piling has already been discussed in Section 17.5, but it is appropriate to revisit it again in the context of detonation.

Considering the simple case of a flame accelerating down a pipe closed at the end distant from the ignition source, the pressure in the gas ahead of the flame may rise due not only to a shock wave close to the flame front but possibly also due to a shock wave reflected from the end of the pipe. It is estimated by Nettleton (1987) that the pressure in the unburned gas may rise by a factor of 2–5.

A separate but related phenomenon is wave interactions associated with the advancing detonation wave. An example is the retonation wave in a pipe closed at the end where ignition occurs. This retonation wave is created at the same time as the detonation wave itself. It travels back through the burned gas, is reflected and then travels forwards again and, since the velocity of sound in the burned gas is much higher than in the unburned gas, overtakes the detonation wave. The latter thus becomes overdriven for a short distance, before it becomes attenuated by the Taylor expansion effect.

17.6.4 Plant design

Essentially, the preferred approach in plant design to the hazard of detonation is prevention rather than protection.

Where an estimate is to be made of the ability of plant to withstand detonation, the approach generally adopted is to use a unidimensional method such as the CJ model. Such models work reasonably well for the simple case of a readily detonable mixture in straight pipe. In any event, there is a lack of a more comprehensive treatment adapted to design.

The traditional approach has been to compare the pressures obtained from a unidimensional model with the static pressures which the plant can withstand. Some of the weaknesses of this approach have been described in Section 17.2. The pressures predicted by unidimensional models are well below those produced by real detonation waves. The method does not take into account the difference between rapidly and slowly applied loads nor the interaction between the shape of the pressure profile and the response time of the confining structure.

The pressures predicted for detonations inside plant tend to be so high that containment is impractical except for certain limited cases such as straight pipes which are of small diameter pipes and/or are open-ended.

However, from an assessment of the limited experimental evidence, Nettleton (1987) concludes that the traditional approach just described appears to be a safe one. The tests were conducted, however, with stoichiometric mixtures for which the detonation pressures are relatively predictable.

With regard to mechanical design, the velocity of an elastic wave in a metal usually exceeds the detonation velocity. This points to separate treatment of the arrivals of the elastic wave and of the detonation wave itself.

In designing against explosions, an approach usually considered is to accept a degree of plastic deformation. A discussion of the planned deformation approach and of the practical problems in implementing it is given by Nettleton (1987). Essentially, it is limited to the early stages of flame acceleration. Nettleton also give guidance on the local strengthening of plant at vulnerable points.

17.6.5 Protection against detonation

Where protection against detonation is to be provided, the preferred approach is to intervene in the processes leading to detonation early rather than late.

Attention is drawn first to the various features which tend to promote flame acceleration, and hence detonation. Minimization of these features therefore assists in inhibiting the development of a detonation. To the extent practical, it is desirable to keep pipelines small in diameter and short; to minimize bends and junctions; and to avoid abrupt changes of cross-section and turbulence promoters.

For protection, the following strategies are described by Nettleton (1987): (1) inhibition of flames of normal burning velocity, (2) venting in the early stages of an explosion, (3) quenching of flame–shock complexes, (4) suppression of a detonation and (5) mitigation of the effects of a detonation.

Methods for the inhibition of a flame at an early stage are described in Chapter 16. Two basic methods are the use of flame arresters and of flame inhibitors.

Flame arresters are described in Section 17.11. The point to be made here is that although an arrester can be effective in the early stages of flame acceleration, siting is critical since there is a danger that in the later stages of a detonation it may act rather as a turbulence generator.

The other method is inhibition of the flame by injection of a chemical. Essentially this involves detection of the flame followed by injection of the inhibitor. At the low flame speeds in the early stage of flame acceleration, there is ample time for detection and injection. The case taken by Nettleton to illustrate this is a gas mixture with a burning velocity of about 1 m/s and expansion ratio of about 10, giving a flame speed of about 10 m/s, for which a separation between detector and injection point of 5 m would give an available time of 0.5 seconds.

In the early stage of an explosion, venting may be an option. The venting of explosion in vessels and pipelines is discussed in Sections 17.12 and 17.13, respectively.

It may be possible in some cases to seek to quench the flame–shock complex just before it has become a fully developed detonation. The methods are broadly similar to those used at the earlier stages of flame acceleration, but the available time is drastically reduced; consequently, this approach is much less widely used. Two examples of such quenching given by Nettleton are the use of packed bed arresters developed for acetylene pipelines in Germany, and widely utilized elsewhere, and the use in coal mines of limestone dust which is dislodged by the flame–shock complex itself.

The suppression of a fully developed detonation may be effected by the use of a suitable combination of an abrupt expansion and a flame arrester. As described earlier, there exists a critical pipe diameter below which a detonation is not transmitted across an abrupt expansion, and this may be exploited to quench the detonation. Work on the quenching of detonations in towns gas using a combination of abrupt expansion and flame arrester has been described by Cubbage (1963).

An alternative method of suppression is the use of water sprays, which may be used in conjunction with an abrupt expansion or without an expansion. The work of Gerstein, Carlson and Hill (1954) has shown that it is possible to stop a detonation using water sprays alone.

17.6.6 Some limitations

There are two principal mechanisms which create pressures which exceed those predicted by the unidimensional models and against which it is difficult to design. One is the pressure piling and wave interaction effects described above which occur during the development of the detonation wave. The other, which applies to the detonation condition itself, arises from instabilities in the combustion behind the leading front. The effects are enhanced in marginally detonable mixtures and by interactions with the confinement.

17.7 Explosions in Closed Vessels

The deflagration of a flammable gas mixture in a closed vessel is important in itself and in relation to venting of the vessel. It is closely related to the combustion of a flammable dust mixture in a vessel. It is also relevant to the measurement of flame speed and of burning velocity.

The two parameters of main interest in explosion in a closed vessel are the maximum pressure P_m and the rate of pressure rise, particularly the maximum rate $(dP/dt)_{max}$.

17.7.1 Energy release and final conditions

As described in Section 17.5, for a deflagration at constant volume in a sphere the maximum explosion pressure is

$$\frac{P_2}{P_1} = \frac{n_2 T_2}{n_1 T_1} \qquad [17.7.1]$$

where n is the number of moles in the gas mixture, P is the absolute pressure, T is the absolute temperature, and the subscripts 1 and 2 denote the initial and final state, respectively. The determination of the maximum pressure therefore involves the calculation of the final temperature.

Combustion in a closed vessel is a constant volume process. The heat of reaction and the gas specific heats applicable to it are those at constant volume. The relevant thermodynamic quantity is the internal energy. Thus the final temperature should be obtained by equating the internal energy of the products to the internal energy of the reactants and the heat of reaction at constant volume.

The computation of the final temperature is frequently done making the incorrect assumption of constant pressure conditions. The problem is discussed by S.M. Richardson, Saville and Griffiths (1990). It is a common, but incorrect, practice to take the final temperature as the adiabatic flame temperature. This is incorrect because the adiabatic flame temperature is a constant pressure quantity. The constant volume flame temperature is appreciably higher.

The aforementioned authors give an example which illustrates the extent of the error. For a stoichiometric mixture of propane and air, which contains 3.98% propane, at initial conditions of pressure 1 bara and temperature 290 K (17°C), the calculated final conditions for adiabatic constant volume combustion are pressure 10.2 bara and temperature 2850 K (2577°C). This compares with values quoted in the literature of final pressure 7.6 bara and temperature 2198 K (1925°C).

The authors state that the difference between the heat of reaction at constant volume and that at constant

pressure is not great. The main source of error lies in the difference between the gas specific heat at constant volume and that at constant pressure.

Thus in constant volume combustion both the final temperature and the final pressure are considerably higher than for combustion at constant pressure.

17.7.2 Experimental studies

There have been a large number of experimental studies of combustion in vessels, both closed and vented. Many of these have been concerned with the venting process, but the proportion of the total work done on closed vessels is appreciable.

Research on combustion in closed vessels has been undertaken for a number of purposes, of which three may be mentioned here. One is the determination of burning velocity. Burning velocity and its measurement have been discussed in Chapter 16. Some models incorporating burning velocity which may be used for its determination are described in this section. Experimental work related to burning velocity includes that of Fiock and Marvin (1937a,b), Fiock *et al.* (1940), Manton, von Elbe and Lewis (1953) and Eschenbach and Agnew (1958).

The second area of work is the investigation of the various factors which influence explosion development in a closed vessel. Here particular mention needs to be made of the extensive programme of work undertaken at the Bureau of Mines (BM), an account of which is given by Nagy and Verakis (1983). It is illustrated by the work of Nagy *et al.* (1971 BM RI 7507) on the effect of variables such as initial pressure, initial temperature, and vessel size and shape. Other work includes that of Kratz and Rosecrans (1922), Ellis and Wheeler (1925, 1928b), Fenning (1926), Rallis, Garforth and Steinz (1965) and G.F.P. Harris (1967).

The third area is studies of detonation, as opposed to deflagration. The BM is again well represented in work in this area, by investigations such as that of Burgess *et al.* (1968 BM RI 7196). Other work includes that of Manson and Ferri (1953) and Pliickebaum, Strauss and Edse (1964).

An account of the findings concerning the effects of the various influencing factors investigated in this work is given below.

One particular outcome of the experimental work may be mentioned at this point. When the flame front reaches a certain radius there is a marked increase in its velocity. At this point the ratio of the pressure to the initial pressure P/P_o becomes strongly influenced by the expansion ratio E.

Plate 15, from the work of R.J. Harris (1983), shows the development of the flame within a vessel with the latter stages influenced by the presence of a vent.

17.7.3 Factors influencing closed vessel explosions

The maximum pressure and the rate of pressure rise in a closed vessel explosion are affected by a number of factors. These are discussed by Bartknecht (1981a), R.J. Harris (1983), Nagy and Verakis (1983) and Lunn (1984b, 1992). They include:

(1) vessel size and shape;
(2) fuel;
(3) fuel–air ratio;
(4) vessel fractional fill;
(5) initial pressure;
(6) initial temperature;
(7) initial turbulence;
(8) ignition source.

A factor which may affect both explosion parameters is heat transfer from the flame and the hot gas to the vessel wall. This can be significant if the vessel has a high aspect, or length/diameter, ratio or if the combustion is relatively slow.

The vessel shape to which most treatments apply is a compact vessel with a length/diameter ratio not exceeding 3. For a compact vessel, maximum pressure is theoretically independent of vessel size and shape if heat transfer is neglected. In practice, maximum pressures tend to show some scatter, but this is random. Maximum pressure it may be less than theoretical if the mixture is slow burning. Mixtures close to the lower explosibility limit tend to burn relatively slowly. The rate of pressure rise does depend on vessel size and shape. The effect of vessel volume is illustrated in Figure 17.10.

In one series of tests it was found that for cubical, rectangular and spherical vessels the rate of pressure rise was proportional to the ratio of the vessel surface S to its volume V. If the vessel shape is such as to promote heat transfer, the rate of pressure rise is reduced.

In an elongated vessel the flame front travels along the axis compressing the unburned gas. The rate of pressure rise is increased compared with that in a more compact vessel. The maximum pressure, however, tends to be less. However, for initial pressures greater than atmospheric, both parameters are enhanced by elongation, as described below.

If the initial pressure is atmospheric, most fuels give a maximum explosion pressure of 8–9 bara.

Both the maximum pressure and rate of pressure rise have maximum values at a fuel concentration close to the stoichiometric value, and decrease as the concentration moves away from this towards the explosibility limits. The effect is shown in Figure 17.11.

If the vessel is only partially filled by the fuel–air mixture, the maximum pressure varies in an approximately linear manner with the fractional fill.

In compact vessels over a limited range of initial pressure the maximum pressure increases linearly with the initial pressure. The rate of rise of pressure is a function of the initial pressure. One set of relations for this are those of Nagy and Verakis which are given below.

In elongated vessels the effect of initial pressure is different, as shown in Figure 17.12, which is for a smaller, spherical vessel and a larger, elongated one. At atmospheric pressure the maximum explosion pressure in the larger vessel is slightly less than that in the smaller one, but at higher initial pressures it is much greater. The maximum rate of pressure rise should be less in the larger vessel, but it is actually higher.

The initial temperature affects the maximum pressure, the rate of pressure rise and the final temperature. The maximum pressure decrease as the initial temperature increases is due to the decrease in density of the fuel–air mixture. The following equation has been used to fit some experimental results

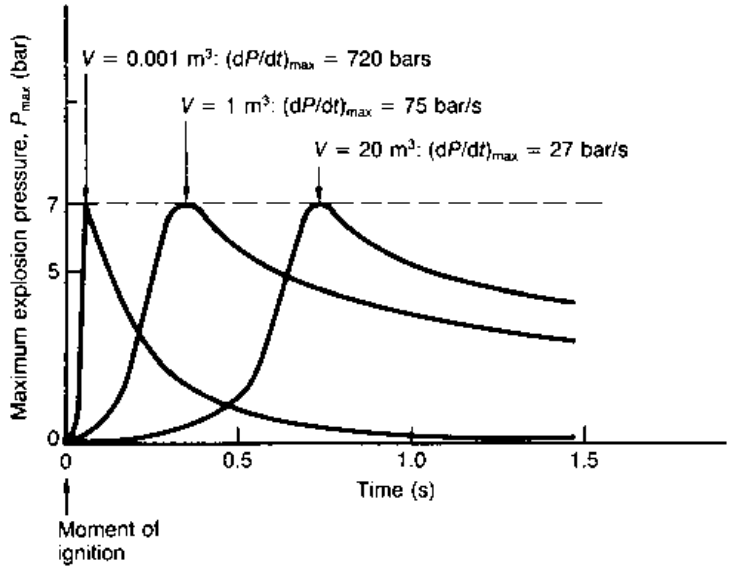

Figure 17.10 *Explosions in closed vessels: effect of vessel volume (Bartknecht, 1981a). Propane at stoichiometric concentration (Courtesy of Elsevier Science)*

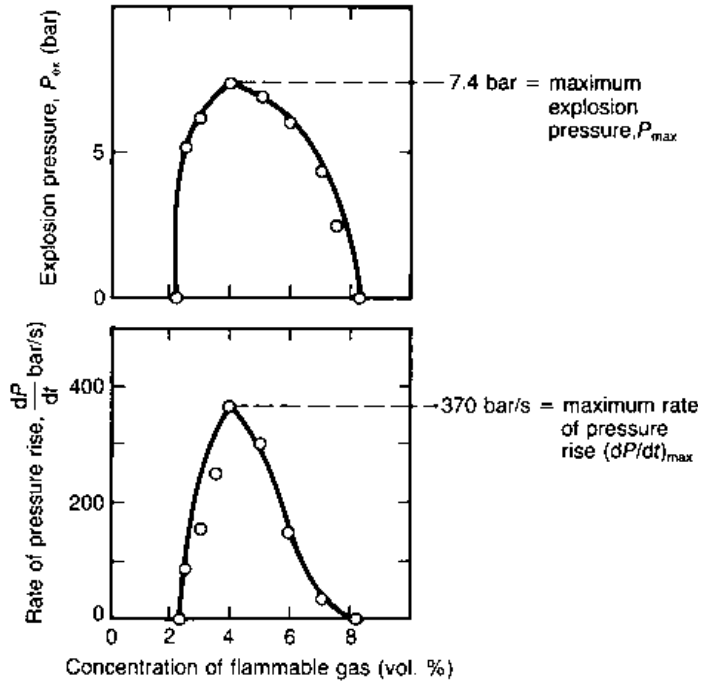

Figure 17.11 *Explosions in closed vessels: effect of gas concentration (Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

$$\frac{P_m}{P_o} = k_1 + \frac{k_2}{T_o} \qquad [17.7.2]$$

where P is the absolute pressure and T is the absolute temperature, the subscripts m and o denote maximum and initial, respectively, and k_1 and k_2 are constants. The rate of pressure rise is essentially independent of the initial temperature, because there are two opposing effects, the lower expansion ratio and the faster burning rate. The final temperature T_e increases linearly with the initial temperature:

$$T_e = k_3 + k_4 T_o \qquad [17.7.3]$$

where k_3 and k_4 are constants.

For compact vessels the initial turbulence has only a slight effect on the maximum pressure, but has a strong effect on rate of pressure rise. This is illustrated in Figure 17.13. Turbulence increases the flame speed. Nagy and Verakis describe experiments on methane–air mixtures where turbulence was created by injecting the fuel–air mixture. In the concentration range 8–12% the effective burning velocity increased by a factor of 5. This factor is generally known as the coefficient of turbulence α. At lower concentrations a value of 8 was obtained for α. For elongated vessels initial turbulence can affect the maximum pressure.

Scheuermann (1994) has described work on the modelling of turbulence relevant to explosions of gas or dust in closed or vented vessels. He correlates the ratio of the laminar and turbulent burning velocities in terms of the velocity component u'.

In a spherical vessel the location of the ignition source has a slight effect on the maximum pressure, but a marked effect on the rate of pressure rise. The rate of pressure rise is greatest for central ignition. The rate of pressure rise increases with the strength of the ignition source.

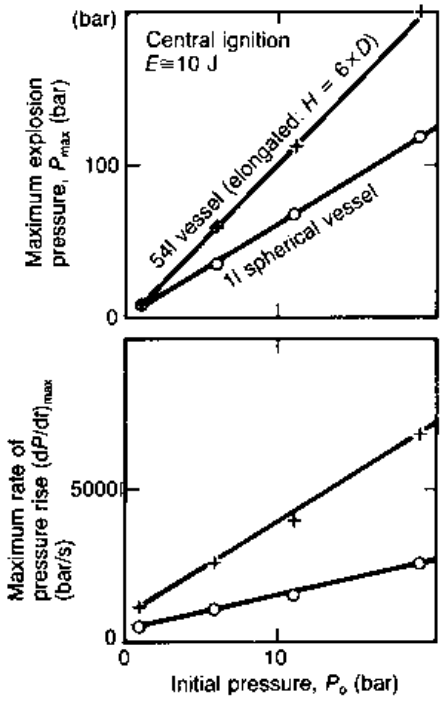

Figure 17.12 *Explosions in closed vessels: effect of initial pressure (Bartknecht, 1981a): methane in a 1 l spherical vessel and in a 54 l elongated vessel (H/D = 6) (Courtesy of Springer-Verlag)*

17.7.4 Modelling of closed vessel explosions

The principal case considered is deflagration in a closed spherical vessel. Treatments of the problem typically produce relations for the pressure P, the rate of change of pressure (dP/dt), the radius r_b of the burned gas core, the rate of change of this radius (dr_b/dt), and the burning velocity S_u.

17.7.5 Elementary relations

These treatments make use of certain common relations and before describing the principal models it is

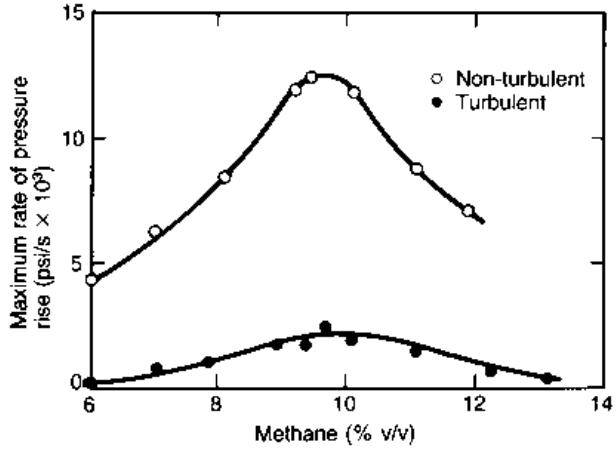

Figure 17.13 *Explosions in closed vessels: effect of initial turbulence (Nagy and Verakis, 1983)*

convenient to give some of these relations. For combustion of a flammable gas mixture in a spherical vessel

$$V_o = V_u + V_b \quad [17.7.4]$$

$$m_o = m_u + m_b \quad [17.7.5]$$

$$m_o = V_o \rho_o \quad [17.7.6]$$

$$m_u = V_u \rho_u \quad [17.7.7]$$

$$m_b = V_b \rho_b \quad [17.7.8]$$

$$n_u = \frac{m_u}{M_u} \quad [17.7.9]$$

$$n_b = \frac{m_b}{M_b} \quad [17.7.10]$$

$$dV_b = -dV_u \quad [17.7.11]$$

$$dm_b = -dm_u \quad [17.7.12]$$

$$V_o = \frac{4\pi a^3}{3} \quad [17.7.13]$$

$$V_i = \frac{4\pi r_i^3}{3} \quad [17.7.14]$$

$$V_b = \frac{4\pi r_b^3}{3} \quad [17.7.15]$$

$$n = \frac{m_b}{m_o} \quad [17.7.16]$$

$$1 - n = \frac{m_u}{m_o} \quad [17.7.17]$$

$$n = \frac{V_i}{V_o} \quad [17.7.18]$$

$$n = \frac{r_i^3}{a^3} \quad [17.7.19]$$

Since some authors work in mass terms and others in molar terms the gas laws are needed in both forms. For mass specific volume v and molar specific volume ν

$$Pv = \frac{RT}{M} \quad [17.7.20a]$$

$$= R_g T \quad [17.7.20b]$$

$$R_g = \frac{R}{M} \quad [17.7.21]$$

$$P\nu = RT \quad [17.7.22]$$

For total volume V

$$PV = \frac{mRT}{M} \quad [17.7.23]$$

$$PV = mR_g T \quad [17.7.24]$$

$$PV = n_j RT \quad [17.7.25]$$

and specifically

$$PV_o = n_o RT \quad [17.7.26]$$

$$PV_u = n_u RT_u \quad [17.7.27]$$

$$PV_b = n_b RT_b \quad [17.7.28]$$

$$\rho = \frac{1}{v} \quad [17.7.29]$$

For compression of the gas

$$Pv^\gamma = \text{constant} \quad [17.7.30]$$

$$P\rho^{-\gamma} = \text{constant} \quad [17.7.31]$$

$$TP^{(1-\gamma)/\gamma} = \text{constant} \quad [17.7.32]$$

$$RTP^{(1-\gamma)/\gamma} = \text{constant} = F \quad [17.7.33]$$

$$PV^{1/\gamma} = \text{constant} = F \quad [17.7.34]$$

For the combustion process

$$A_f = 4\pi r_b^2 \quad [17.7.35]$$

$$\frac{dV_b}{dr_b} = A_f \quad [17.7.36]$$

$$\frac{dm_b}{dt} = A_f \rho_u S_u \quad [17.7.37]$$

$$\frac{dr_b}{dt} = S_f \quad [17.7.38]$$

$$S_f = u_u + S_u \quad [17.7.39]$$

$$S_f = E S_u \quad [17.7.40]$$

$$E = \frac{\rho_u}{\rho_b} \quad [17.7.41]$$

where a is the radius of the spherical vessel, A_f is the area of the flame front, E is the expansion ratio, m is the mass of gas, M is the molecular weight, n is the fractional degree of combustion, n (with subscript) is the number of moles of gas, P is the absolute pressure, r is the radius, R is the universal gas constant, R_g is the mass basis gas constant, S_f is the flame speed, S_u is the burning velocity, t is time, T is the absolute temperature, u_u is the velocity of the unburned gas into the flame front, v is the specific mass volume of the gas, V is the total volume, γ is the ratio of gas specific heats, ν is the specific molar volume of the gas, ρ is the mass density and the subscripts b, o, and u denote burned, initial and unburned, respectively. V_o is the volume of the vessel and m_o the mass of gas in the vessel. The subscript i refers to the initial state of the burned gas and j to any gas state.

Use is also made of the approximations

$$r_b = S_f t \quad [17.7.42]$$

$$E^2(E-1) = E^3 \quad [17.7.43]$$

17.7.6 Zabetakis model

Zabetakis (1965 BM Bull. 627) has given the following equation for the pressure rise resulting from combustion in a closed spherical vessel:

$$\frac{\Delta P}{P_o} = \frac{K S_u^3 t^3}{V} \quad [17.7.44]$$

with

$$\Delta P = P - P_o \quad [17.7.45]$$

where K is a constant. Hence

$$\frac{P}{P_o} = 1 + \frac{K S_u^3 t^3}{V} \quad [17.7.46]$$

According to Nagy and Verakis, Equation 17.7.44 is in the first instance an empirical one, but both they and other workers have derived it theoretically, as described below.

Differentiating Equation 17.7.46 gives

$$\frac{dP}{dt} = \frac{3 K P_o S_u^3 t^2}{V} \quad [17.7.47]$$

For a given explosion pressure $t \propto V^{1/3}$ and hence

$$\left(\frac{dP}{dt}\right) V^{\frac{1}{3}} = \text{constant} \quad [17.7.48a]$$

$$= K_G \quad [17.7.48b]$$

Equation 17.7.48 is usually applied to $(dP/dt)_{max}$ but it is strictly applicable only where (dP/dt) is measured at the same pressure in each volume.

17.7.7 Flamm and Mache model

In one of the earliest treatments of the problem, Flamm and Mache (1917) derived the equation

$$1 - n = \frac{R T_o}{R T_u (\gamma_b - \gamma_u)/(\gamma_u - 1) + K(\gamma_b - 1)} \frac{P_e - P}{P_o} \quad [17.7.49]$$

where K is a constant and the subscript e denotes the end.

17.7.8 Fiock and Marvin model

Fiock and Marvin (1937a,b) derived the following equation for the burning velocity:

$$S_u = \frac{dr_b}{dt} - \frac{a^3 - r_b^3}{3 P \gamma_u r_b^2} \frac{dP}{dt} \quad [17.7.50]$$

17.7.9 Lewis and von Elbe model

Another early treatment was that of B. Lewis and von Elbe (1951) (also Manton, von Elbe and Lewis, 1953). Starting with Equation 17.7.33 and the relation

$$V_o = \frac{R}{P}\left(n_e \int_0^n T_{bP}\, dn + n_o T_u (1 - n)\right) \quad [17.7.51]$$

where T_{bP} is the absolute temperature corresponding to pressure P, they derive Equation 17.7.49 of Flamm and Mache.

Then from Equation 17.7.49 for $n = 0$, $T_u = T_o$ and $P = P_o$ and noting that for practical cases

$$R T_o (\gamma_b - \gamma_u)/(\gamma_u - 1) \ll K(\gamma_b - 1) \quad [17.7.52]$$

they derive the following approximation

$$n = \frac{P - P_o}{P_e - P_o} \quad [17.7.53]$$

Equation 17.7.53 is often used in the differential form

$$\frac{dn}{dt} = \frac{1}{P_e - P_o} \frac{dP}{dt} \quad [17.7.54]$$

For the burned gas core they define two radii: r_i the radius before ignition of the gas and r_b the radius after expansion. Then, utilizing Equation 17.7.19 for the radius before expansion

$$r_i = a\left(\frac{P - P_o}{P_e - P_o}\right)^{\frac{1}{3}} \quad [17.7.55]$$

and utilizing Equations 17.7.17 and 17.7.27 for the radius after expansion

$$V_u = \frac{n_o R T_u (1 - n)}{P} \quad [17.7.56]$$

$$r_b = a\left(1 - \frac{P_o T_u}{P T_o}(1 - n)\right)^{\frac{1}{3}} \quad [17.7.57]$$

$$r_b = a\left[1 - \frac{P_o T_u}{P T_o}\left(\frac{P_e - P}{P_e - P_o}\right)\right]^{\frac{1}{3}} \quad [17.7.58]$$

with

$$T_u = T_o \left(\frac{P}{P_o}\right)^{(\gamma_u - 1)/\gamma_u} \quad [17.7.59]$$

For the burning velocity, the volume of an element of the shell of the burned gas core before expansion is

$$4\pi r_i^2\, dr_i \quad [17.7.60]$$

at P_i and T_i, and the volume after expansion is

$$4\pi r_i^2\, dr_i \left(\frac{T_u P_o}{T_o P}\right) \quad [17.7.61]$$

But this volume is also equal to

$$4\pi r_b^2 S_u\, dt \quad [17.7.62]$$

Equating Equations 17.7.61 and 17.7.62 and applying Equation 17.7.59

$$S_u = \left(\frac{r_i}{r_b}\right)^2 \left(\frac{P_o}{P}\right)^{1/\gamma_u} \frac{dr_i}{dt} \quad [17.7.63]$$

17.7.10 O'Donovan and Rallis model

The following treatment by O'Donovan and Rallis (1959) supplements those of the last two sets of workers. From Equations 17.7.17, 17.7.24 and 17.7.32

$$V_u = V_o (1 - n)\left(\frac{P_o}{P}\right)^{1/\gamma_u} \quad [17.7.64]$$

From Equations 17.7.15 and 17.7.64

$$V_b = V_o \left[1 - (1 - n)\left(\frac{P_o}{P}\right)^{1/\gamma_u}\right] \quad [17.7.65]$$

$$r_b = a\left[1 - (1 - n)\left(\frac{P_o}{P}\right)^{1/\gamma_u}\right]^{\frac{1}{3}} \quad [17.7.66]$$

or rearranging Equation 17.7.66

$$n = 1 - \left(1 - \frac{r_b^3}{a^3}\right)\left(\frac{P_o}{P}\right)^{1/\gamma_u} \quad [17.7.67]$$

Equating the volume rate of change of the unburned gas passing through the flame front with that of the unburned gas in its actual state of adiabatic compression

$$4\pi r_b^2 S_u = 4\pi r_i^2 \left(\frac{dr_i}{dt}\right)\left(\frac{T_u P_o}{T_o P}\right) \quad [17.7.68]$$

Hence

$$S_u = \frac{dr_i}{dt}\left(\frac{r_i}{r_b}\right)^2 \left(\frac{P_o}{P}\right)^{1/\gamma_u} \quad [17.7.69]$$

Also from Equation 17.7.19

$$\frac{dn}{dt} = \frac{3r_i^2}{a^3}\frac{dr_i}{dt} \quad [17.7.70]$$

From Equations 17.7.69 and 17.7.70

$$S_u = \frac{a^3}{3r_b^2}\left(\frac{P_o}{P}\right)^{1/\gamma_u}\frac{dn}{dt} \quad [17.7.71]$$

Then noting that in Equation 17.7.67 both r_b and P are functions of time and differentiating n in that equation with respect to t and substituting for dn/dt in Equation 17.7.71 gives Equation 17.7.50 of Fiock and Marvin.

17.7.11 Nagy and Verakis model

Nagy and Verakis (1983) give treatments for both isothermal and adiabatic cases. Their starting point is the rate of production of the burned mass. Assuming $M_b = M_u$,

$$\frac{dn_b}{dt} = \frac{\alpha A_f S_u P}{RT_u} \quad [17.7.72]$$

where α is a flame area factor which allows for the difference between the nominal area of the flame front and the actual area, which is higher due to flame wrinkling.

For the isothermal case

$$\frac{T_u}{T_b} = \frac{P_o}{P_e} \quad [17.7.73]$$

From Equations 17.7.27 and 17.7.28, differentiating with respect to t and assuming $M_b = M_u$ so that $dn_u/dt = -dn_b/dt$

$$V\frac{dP}{dt} = \frac{dn_b}{dt}(RT_b - RT_u) \quad [17.7.74]$$

From Equations 17.7.72–17.7.74

$$\frac{dP}{dt} = \frac{\alpha A_f S_u P(P_e - P_o)}{VP_o} \quad [17.7.75]$$

In order to integrate Equation 17.7.75 it is necessary to express A_f as a function of P. From Equations 17.7.15 and 17.7.35

$$A_f = 4\pi\left(\frac{3V_b}{4\pi}\right)^{\frac{2}{3}} \quad [17.7.76]$$

and from Equations 17.7.5, 17.7.9, 17.7.10, 17.7.27 and 17.7.28 and again assuming $M_b = M_u$ so that $n_o = n_u + n_b$

$$V_b = V\frac{1 - P_o/P}{1 - P_o/P_e} \quad [17.7.77]$$

From Equations 17.7.75, 17.7.76 and 17.7.77

$$\frac{dP}{dt} = \frac{\alpha S_u P_e^{\frac{2}{3}}}{VP_o}(P_e - P_o)^{\frac{1}{3}}(1 - P_o/P)^{\frac{2}{3}}P \quad [17.7.78]$$

Integration of Equation 17.7.78 is difficult, but an approximate solution over a limited range is

$$P = P_o + (P_e - P_o)\left(\frac{P_e}{P_o}\right)^2\left(\frac{\alpha S_u t}{3V}\right)^3 \qquad P_o \le P \le 2P_o \quad [17.7.79]$$

Equation 17.7.79 is similar to Equation 17.7.46 of Zabetakis. Equating the two equations gives the value of the constant K in the latter equation as

$$K = \frac{4}{3}\frac{\pi}{P_o}(P_e - P_o)\left(\frac{P_e}{P_o}\right)^2 \quad [17.7.80]$$

The authors also treat the adiabatic case, which leads to rather complex relationships.

17.7.12 Model of Perlee, Fuller and Saul

Perlee, Fuller and Saul (1974 BM RI 7839) have derived Equation 17.7.46 and have determined the value of the constant K. Differentiating Equation 17.7.27 with respect to n_u and Equation 17.7.28 with respect to n_b

$$V_u\,dP + P\,dV_u = RT_u\,dn_u + Rn_u\,dT_u \quad [17.7.81]$$

$$V_b\,dP + P\,dV_b = RT_b\,dn_b + Rn_b\,dT_b \quad [17.7.82]$$

Hence

$$dP[V_o(1 - \alpha_u) + V_b(\alpha_u - \alpha_b)] = -R\left[T_b - T_u\left(\frac{M_b}{M_u}\right)\right]dn_u \quad [17.7.83]$$

with

$$\alpha_u = \frac{\gamma_u - 1}{\gamma_u} \quad [17.7.84]$$

$$\alpha_b = \frac{\gamma_b - 1}{\gamma_b} \quad [17.7.85]$$

But from Equations 17.7.9, 17.7.12, 17.7.35 and 17.7.37

$$\frac{dn_u}{dt} = -4\pi r_b^2\frac{\rho_u S_u}{M_u} \quad [17.7.86]$$

Then from Equations 17.7.83 and 17.7.86

$$\frac{dP}{dt} = \frac{3\gamma_u P(E-1)S_u r_b^2}{a^3 + r_b^3\left(\frac{\gamma_u}{\gamma_b} - 1\right)} \quad [17.7.87]$$

with E as defined by Equation 17.7.41 or alternatively

$$E = \frac{M_u T_b}{M_b T_u} \quad [17.7.88]$$

Then from Equations 17.7.40, 17.7.42 and 17.7.87

$$\frac{\mathrm{d}\ln P}{\mathrm{d}t} = \frac{3\gamma_u(E-1)}{a}\left(\frac{S_u E t}{a}\right)^2 S_u \quad [17.7.89]$$

Integrating Equation 17.7.89

$$\ln\left(\frac{P}{P_o}\right) = \gamma_u E^2(E-1)\left(\frac{S_u}{a}\right)^3 t^3 \quad [17.7.90]$$

Introducing the approximation

$$\ln\left(\frac{P_o + \Delta P}{P_o}\right) \approx \frac{\Delta P}{P_o} \quad [17.7.91]$$

$$\frac{\Delta P}{P_o} = \gamma_u E^2(E-1)\left(\frac{S_u}{a}\right)^3 t^3 \quad [17.7.92]$$

$$= \frac{K S_u^3 t^3}{V} \quad [17.7.93]$$

with

$$K = \frac{4}{3}\pi E^2(E-1)\gamma_u \quad [17.7.94]$$

17.7.13 Harris model

An alternative relation for the rate of pressure rise is derived by R.J. Harris (1983). From Equations 17.7.8 and 17.7.37

$$V_b\frac{\mathrm{d}\rho_b}{\mathrm{d}t} + \rho_b\frac{\mathrm{d}V_b}{\mathrm{d}t} = A_f\rho_u S_u \quad [17.7.95]$$

Then from Equations 17.7.36, 17.7.38 and 17.7.95

$$V_b\frac{\mathrm{d}\rho_b}{\mathrm{d}t} + \rho_b A_f S_f = A_f\rho_u S_u \quad [17.7.96]$$

But initially $\mathrm{d}P/\mathrm{d}t$ is small and so is $\mathrm{d}\rho_b/\mathrm{d}t$. Hence from Equation 17.7.96

$$S_f = \left(\frac{\rho_u}{\rho_b}\right)S_u \quad [17.7.97]$$

$$= E S_u \quad [17.7.98]$$

Equation 17.7.98 may be modified to take account of the increase in area of the flame front due to turbulence by introducing a coefficient of turbulence α

$$S_f = \alpha E S_u \quad [17.7.99]$$

Initially when the pressure rise is low, it is possible to make the assumption that T_u and T_b are constant, termed by the author the isothermal assumption. Then differentiating Equations 17.7.27 and 17.7.28 and adding the resulting equations and utilizing Equations 17.7.4 and 17.7.12 gives

$$V\frac{\mathrm{d}P}{\mathrm{d}t} = \left(\frac{RT_b}{M_b} - \frac{RT_u}{M_u}\right)\frac{\mathrm{d}m_b}{\mathrm{d}t} \quad [17.7.100]$$

From Equations 17.7.7, 17.7.37 and 17.7.100

$$V\frac{\mathrm{d}P}{\mathrm{d}t} = A_f P(E-1)S_u \quad [17.7.101]$$

From Equations 17.7.35, 17.7.40, 17.7.42 and 17.7.101

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{4\pi P S_u^3 E^2(E-1)t^2}{V} \quad [17.7.102]$$

Integrating Equation 17.7.102

$$\frac{P}{P_o} = \exp\left(\frac{4\pi E^2(E-1)(S_u t)^3}{3V}\right) \quad [17.7.103]$$

For a spherical vessel

$$\frac{P}{P_o} = \exp\left(\frac{E^2(E-1)}{a^3}(S_u t)^3\right) \quad [17.7.104]$$

17.7.14 Bradley and Mitcheson model

D. Bradley and Mitcheson (1976) derive what they call a universal expression for the rate of pressure rise. From Equations 17.7.7, 17.7.12 and 17.7.37 they obtain for the unburned gas

$$\frac{\mathrm{d}[(a^3 - r_b^3)\rho_u]}{\mathrm{d}t} = -3r_b^2\rho_u S_u \quad [17.7.105]$$

and for the burned gas

$$\frac{\mathrm{d}(r_b^3\rho_b)}{\mathrm{d}t} = 3r_b^2\rho_u S_u \quad [17.7.106]$$

From Equations 17.7.31 and 17.7.105 it can be shown that

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{3r_b^2\gamma_u P}{a^3 - r_b^3}\left(\frac{\mathrm{d}r_b}{\mathrm{d}t} - S_u\right) \quad [17.7.107]$$

which can be rearranged to give Equation 17.7.50 of Fiock and Marvin (1937a,b).

From Equations 17.7.4, 17.7.5, 17.7.7, 17.7.12, 17.7.27, 17.7.31, 17.7.35 and 17.7.37 Bradley and Mitcheson derive

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{3S_u\rho_u}{a\rho_o}(P_e - P_o)\left[1 - \left(\frac{P_o}{P}\right)^{1/\gamma_u}\frac{P_e - P}{P_e - P_o}\right]^{\frac{2}{3}} \quad [17.7.108]$$

They also give Equation 17.7.108 in dimensionless form and describe it as the dimensionless universal equation.

17.7.15 Morton and Nettleton model

Morton and Nettleton (1977) give the following treatment. Consider an element of the burned gas shell of inner radius r and outer radius $r + \delta r$. If the shell is moving with velocity $u(r)$, then after time δt the inner radius is equal to

$$r + u\,\mathrm{d}t \quad [17.7.109]$$

and the outer radius to

$$r + \delta r + \left(u + \frac{\mathrm{d}u}{\mathrm{d}r}\delta r\right)\mathrm{d}t \quad [17.7.110]$$

The initial volume of the element is

$$V = 4\pi r^2\,\delta r \quad [17.7.111]$$

After time $\mathrm{d}t$ the area of the shell is

$$4\pi(r + u\,\mathrm{d}t)^2 \quad [17.7.112]$$

and the thickness is

$$\left\{r+\delta r+\left[u+\left(\frac{\mathrm{d}u}{\mathrm{d}t}\delta r\right)\right]\mathrm{d}t\right\}-(r+u\,\mathrm{d}t) \qquad [17.7.113a]$$

or

$$\delta r\left(1+\frac{\mathrm{d}u}{\mathrm{d}r}\mathrm{d}t\right) \qquad [17.7.113b]$$

Subtracting the initial volume given by Equation 17.7.111 from the volume after the time increment dt given by Equations 17.7.112 and 17.7.113 gives

$$\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}t}=\frac{\mathrm{d}u}{\mathrm{d}t}+\frac{2u}{r^2} \qquad [17.7.114]$$

By logarithmic differentiation of Equation 17.7.30

$$\frac{1}{P}\frac{\mathrm{d}P}{\mathrm{d}t}=-\gamma\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}t} \qquad [17.7.115]$$

Hence from Equations 17.7.114 and 17.7.115

$$\frac{1}{P}\frac{\mathrm{d}P}{\mathrm{d}t}=-\gamma\left(\frac{\mathrm{d}u}{\mathrm{d}r}+\frac{2u}{r}\right) \qquad [17.7.116]$$

Integrating Equation 17.7.116 with the boundary conditions

$$r=a;\ u_1=0 \qquad [17.7.117a]$$

$$r=0;\ u_2=0 \qquad [17.7.117b]$$

where the subscripts 1 and 2 denote unburned gas and burned gas, respectively, gives

$$u_1=\frac{1}{3\gamma_1 P}\left(\frac{a^3-r^3}{r^2}\right)\frac{\mathrm{d}P}{\mathrm{d}t} \qquad [17.7.118]$$

$$u_2=\frac{r}{3\gamma_2 P}\frac{\mathrm{d}P}{\mathrm{d}t} \qquad [17.7.119]$$

Now consider a stationary flame front with a flow of unburned mixture into the front and of burned mixture away from the front. By conservation of mass

$$u_1-u_2=E-1 \qquad [17.7.120]$$

From the definition of burning velocity S_u

$$\frac{\mathrm{d}r}{\mathrm{d}t}=u_1+S_u \qquad [17.7.121]$$

From Equations 17.7.118 and 17.7.121

$$\frac{\mathrm{d}P}{\mathrm{d}t}=\frac{3\gamma_1 Pr^2}{a^3-r^3}\left(\frac{\mathrm{d}r}{\mathrm{d}t}-S_u\right) \qquad [17.7.122]$$

From Equations 17.7.118, 17.7.119 and 17.7.120

$$\frac{\mathrm{d}P}{\mathrm{d}t}=\frac{3\gamma_1 Pr^2 S_u(E-1)}{a^3-(1-\gamma_1/\gamma_2)r^3} \qquad [17.7.123]$$

Equating Equations 17.7.122 and 17.7.123 gives

$$\frac{\mathrm{d}r}{\mathrm{d}t}=\frac{ES_u[a^3-(1-\gamma_1/E\gamma_2)r^3]}{[a^3-(1-\gamma_1/\gamma_2)r^3]} \qquad [17.7.124]$$

Then from Equations 17.7.123 and 17.7.124

$$\frac{\mathrm{d}P}{\mathrm{d}t}=\frac{E-1}{E}\frac{3\gamma_1 Pr^2}{a^3-(1-\gamma/E\gamma_2)r^3}\frac{\mathrm{d}r}{\mathrm{d}t} \qquad [17.7.125]$$

Integrating Equation 17.7.125 with the boundary condition

$$r=0;\ P=P_o \qquad [17.7.126]$$

gives

$$\frac{P}{P_o}=\left(\frac{a^3}{a^3-(1-\gamma_1/E\gamma_2)r^3}\right)^{\gamma_1(E-1)/(E-\gamma_1/\gamma_2)} \qquad [17.7.127]$$

The authors point out that their model is not formulated in terms of the rate of flame spread. It gives the maximum pressure as a function of the expansion ratio, but not explicitly of the burning velocity. However, the expansion ratio increases with burning velocity, since it increases with flame temperature, which in turn increases with burning velocity.

17.7.16 Fairweather and Vasey model

The treatment by Fairweather and Vasey (1982) makes allowance for two features not usually taken into account. One is the fact that due to the existence of dissociation reactions the polytropic assumption, though valid for the unburned gas, is not valid for the burned gas. The other is heat loss to the vessel by radiation. They give the heat balance

$$m_u U_u+m_b U_b-Q=m_o C_n-m_u C_n \qquad [17.7.128]$$

with

$$U_u=\frac{R(T_u-T_o)}{(\gamma_u-1)M_u} \qquad [17.7.129]$$

$$U_b=h_b-\frac{R(T_b-T_{<o})}{M_b} \qquad [17.7.130]$$

where C_n is the calorific value of the mixture, h is the enthalpy, Q is the thermal energy lost from the burned products and U is the internal energy.

17.7.17 Singh model

The foregoing models are for spherical vessels. A treatment which covers cylindrical geometries also has been given by J. Singh (1988b). From Equations 17.7.7, 17.7.12 and 17.7.37

$$\frac{\mathrm{d}P}{\mathrm{d}t}=-A_f S_u\left(\frac{\mathrm{d}V_u}{\mathrm{d}P}+\frac{V_u}{\rho_u}\frac{\mathrm{d}\rho_u}{\mathrm{d}P}\right)^{-1} \qquad [17.7.131]$$

By logarithmic differentiation of Equation 17.7.31

$$\frac{\mathrm{d}\rho}{\mathrm{d}P}=\frac{\rho}{\gamma P} \qquad [17.7.132]$$

Hence from Equations 17.7.131 and 17.7.132

$$\frac{\mathrm{d}P}{\mathrm{d}t}=-A_f S_u\left(\frac{V_u}{\gamma_u P}+\frac{\mathrm{d}V_u}{\mathrm{d}P}\right)_{-1} \qquad [17.7.133]$$

Equations 17.7.6, 17.7.7, 17.7.17 and 17.7.31, writing the latter in the form

$$\frac{\rho_o}{\rho_u}=\left(\frac{P_o}{P}\right)^a \qquad [17.7.134]$$

with

$$a = \frac{1}{\gamma_u} \quad [17.7.135]$$

yield

$$V_u = V_o(1-n)\left(\frac{P_o}{P}\right)^a \quad [17.7.136]$$

Differentiating Equation 17.7.136 with respect to P and combining the result with Equation 17.7.133 gives

$$\frac{dP}{dt} = \frac{A_f S_u}{V_o}\left(\frac{P_o}{P}\right)^{-a}\left(\frac{dn}{dP}\right)^{-1} \quad [17.7.137]$$

In order to solve Equation 17.7.137 it is necessary to have a relation between P and n. A simple approach is to use Equations 17.7.4, 17.7.6, 17.7.8 and 17.7.16, which gives

$$V_u = V_o(1 - n/\alpha) \quad [17.7.138]$$

with

$$\alpha = \rho_b/\rho_o \quad [17.7.139]$$

Then from Equations 17.7.136 and 17.7.138

$$n = \alpha\left(\frac{(P/P_o)^a - 1}{(P/P_o)^a - \alpha}\right) \quad [17.7.140]$$

There remains, however, a difficulty in that ρ_b, and hence α, varies throughout the burnt gas region. Again it is necessary to adopt a simplified approach. From Equations 17.7.20a and 17.7.29 for the burnt gas

$$\rho_b = \left(\frac{\bar{M}_b P}{R\bar{T}_b}\right) \quad [17.7.141]$$

and for gas at the end of combustion

$$\rho_e = \left(\frac{\bar{M}_e P_e}{R\bar{T}_e}\right) \quad [17.7.142]$$

where $\bar{M}$ is the mean molecular weight.

Hence from Equation 17.7.139 and noting that $\rho_o = \rho_e$

$$\alpha = \left(\frac{\bar{M}_b \bar{T}_e P}{\bar{M}_e \bar{T}_b P_e}\right) \quad [17.7.143]$$

One simplification of Equation 17.7.143, where $\bar{M}_b \simeq \bar{M}_e$, is

$$\alpha = \left(\frac{\bar{T}_e P}{\bar{T}_b P_e}\right) \quad [17.7.144]$$

In fact the values of n obtained from Equation 17.7.144 differ only slightly from those obtained from the further simplification

$$\alpha = \frac{P}{P_e} \quad [17.7.145]$$

Then from Equations 17.7.140 and 17.7.145

$$n = \left(\frac{P}{P_e}\right)\left(\frac{(P/P_o)^a - 1}{(P/P_o)^a - (P/P_e)}\right) \quad [17.7.146]$$

So far the treatment is general with respect to vessel geometry. For a specific geometry it is necessary to characterize the area of the flame front A_f. Consider first combustion in a spherical vessel. For this case

$$\left(\frac{r_b}{r_s}\right)^3 = \left(\frac{V_b}{V_o}\right) \quad [17.7.147]$$

where r_s is the radius of the vessel. Combining Equations 17.7.4, 17.7.136 and 17.7.147

$$r_b = r_s\left[1 - (1-n)\left(\frac{P_o}{P}\right)^a\right]^{\frac{1}{3}} \quad [17.7.148]$$

From Equation 17.7.137

$$S_u = \frac{V_o}{A_f}\left(\frac{P_o}{P}\right)^a\left(\frac{dn}{dP}\right)\left(\frac{dP}{dt}\right) \quad [17.7.149]$$

Then from Equations 17.7.148 and 17.7.149

$$S_u = \frac{r_s(P_o/P)^a}{3[1-(1-n)(P_o/P)^a]^{\frac{2}{3}}}\left(\frac{dn}{dP}\right)\left(\frac{dP}{dt}\right) \quad [17.7.150]$$

For combustion in a cylindrical vessel Singh considers a vessel length L and radius r_c, where $L > r_c$. He distinguishes between central ignition and end ignition, and for each of these cases takes a two-stage approach. For combustion in a cylindrical vessel with central ignition he gives the following treatment. Initially the flame expands symmetrically in all directions. When the radius r_b of the flame is approximately equal to the radius r_c of the vessel, the flames begins to distort. It is assumed that the flame front then separates into two parts and that these two parts of the flame front then travel as two hemispherical shells of radius r_c in opposite directions until they reach the ends of the cylinder. For the first stage of this process substituting for n from Equation 17.7.146 into Equation 17.7.150 gives

$$\frac{d\bar{P}}{d\bar{t}} = G_1\bar{P}^a\left\{1 - \bar{P}^{-a}\left[1 - \frac{\bar{P}}{\bar{P}_e}\left(\frac{\bar{P}^a - 1}{\bar{P}^a - \bar{P}/\bar{P}_e}\right)\right]\right\}^{\frac{2}{3}}\left(\frac{dn}{d\bar{P}}\right)^{-1} \quad [17.7.151]$$

and

$$\frac{dn}{d\bar{P}} = \left[\left(\frac{\bar{P}}{\bar{P}_e}\right)\frac{a(\bar{P} - \bar{P}/\bar{P}_e)\bar{P}^{a-1} - (\bar{P}^a - 1)(a\bar{P}^{(a-1)} - 1/\bar{P}_e}{(\bar{P}^a - \bar{P}/\bar{P}_e)^2}\right] + \left[\frac{1}{\bar{P}_e}\left(\frac{\bar{P}^{-a} - 1}{\bar{P}^a - \bar{P}/\bar{P}_e}\right)\right] \quad [17.7.152]$$

with

$$\bar{P} = \frac{P}{P_o} \quad [17.7.153]$$

$$\bar{P}_e = \frac{P_e}{P_o} \quad [17.7.154]$$

$$\bar{t} = \frac{tS_u}{r_s} \quad [17.7.155]$$

$$G_1 = 3 \quad [17.7.156]$$

where the overbar denotes dimensionless. Transition from the first stage to the second stage occurs at pressure $\bar{P}_x$ such that

$$r_b = G_2 r_s \left(\frac{\bar{P}_x^a - 1}{\bar{P}_x^a - \bar{P}_x/\bar{P}_e} \right)^{\frac{1}{3}} \quad [17.7.157a]$$

$$= r_c \quad [17.7.157b]$$

with

$$G_2 = 1 \quad [17.7.158]$$

where now r_s is the radius of the sphere equal in volume to the cylinder. Hence

$$r_s = \left(\frac{3r_c^2 L}{4} \right)^{\frac{1}{3}} \quad [17.7.159]$$

For the second stage the total flame area is

$$A_f = 4\pi r_c^2 \quad [17.7.160]$$

Also

$$V_o = \pi r_c^2 L \quad [17.7.161]$$

Then from Equations 17.7.53, 17.7.137, 17.7.160 and 17.7.161

$$\frac{dP}{dt} = \frac{4S_u}{L}(P_e - P_o)\left(\frac{P_o}{P} \right)^{-a} \quad [17.7.162]$$

Integrating Equation 17.7.162 gives

$$\bar{t} = \frac{(L/r_s)\bar{P}^{1-a}}{G_3(\bar{P}_e - 1)(1-a)} + \frac{S_u K_1}{r_s} \quad [17.7.163]$$

with

$$G_3 = 4 \quad [17.7.164]$$

for central ignition. The constant K_1 satisfies the condition that transition occurs at time $\bar{t}_x$ where the latter is obtained from Equation 17.7.151.

The treatment for a cylindrical vessel with end ignition is similar. In this case

$$\left(\frac{r_b}{r_s} \right)^3 = \left(\frac{2V_b}{V_o} \right) \quad [17.7.165]$$

and hence

$$r_b = 2^{\frac{1}{3}} r_s \left[1 - (1-n)\left(\frac{P_o}{P} \right)^a \right]^{\frac{1}{3}} \quad [17.7.166]$$

Equations 17.7.151 and 17.7.157 apply but with

$$G_1 = 3/2^{\frac{1}{3}} \quad [17.7.167]$$

$$G_2 = 2^{\frac{1}{3}} \quad [17.7.168]$$

For the second stage the total area of the flame is

$$A_f = 2\pi r_c^2 \quad [17.7.169]$$

Hence

$$\frac{dP}{dt} = \frac{2S_u}{L}(P_e - P_o)\left(\frac{P_o}{P} \right)^{-a} \quad [17.7.170]$$

For transition, Equation 17.7.163 applies but with

$$G_3 = 2 \quad [17.7.171]$$

17.8 Explosions in Buildings

Many process plants are in buildings. It is also necessary, therefore, to consider explosions occurring inside buildings.

A leak of flammable gas or liquid may create a flammable atmosphere inside a building and give rise to an explosion. Such leaks may occur from plant processing flammable fluids, from activities involving such fluids or from fuel gas supplies. In enclosed conditions, dispersion of the leaked gas is poor and the hazard is therefore much enhanced.

An area of prime concern in respect of explosions in buildings is the hazard of gas explosions in dwellings, and much of the work done relates to this. An account is given in *Gas Explosions in Buildings and Heating Plant* (R.J. Harris, 1983).

17.8.1 Building explosion incidents

Statistical information on the hazard of explosions in buildings has been given by F. Morton (1970), Mainstone (1973 BRE CP 11/73; 1974 BRE BR9; 1983 BRE CP 2/83) and by Taylor and Alexander (1974 BRE CP 45/74).

A number of case histories of building explosions have been described by Mainstone (1976 BRE CP 24/76). One of the most severe building explosions was that at Ronan Point in 1968, which was the subject of an official report (H. Griffiths *et al.*, 1968).

Analyses of the factors bearing on gas explosions in buildings have been given by Mainstone (1973 BRE CP 11/73; 1976 BRE CP 24/76) and by Taylor and Alexander (1974 BRE CP 45/74)

17.8.2 Ventilation of buildings

Movement of air in a building may be due to natural or to forced draught ventilation. Natural draught ventilation may be either thermal driven or wind driven. In the former case the movement of air is caused by the temperature difference between the inside and the outside of the building, while in the latter it caused by the pressure of the wind on the side of the building.

General guidance on natural ventilation is given in BS 5925: 1991 *Code of Practice: Ventilation Principles and Designing for Natural Ventilation*. Typical natural ventilation rates are in the range 0.5–3 air changes/h.

Guidance on ventilation in relation to flammable and toxic gases is given by Leach and Bloomfield (1973, 1974 BRE CP 36/74).

For forced draught ventilation, guidance is given in BS 5720: 1979 *Code of Practice for Mechanical Ventilation and Air Conditioning in Buildings*. Forced draught ventilation is provided by fans. With forced draught ventilation rates can be not only higher but more dependable.

Human comfort sets a limit to the ventilation rate which can be used under normal conditions. A typical rule of thumb is that the upper limit of the air velocity for comfort is about 0.5 m/s.

There is no reason, however, why the ventilation rate should be limited to a low level in an emergency. In such a situation additional ventilation may be brought into play.

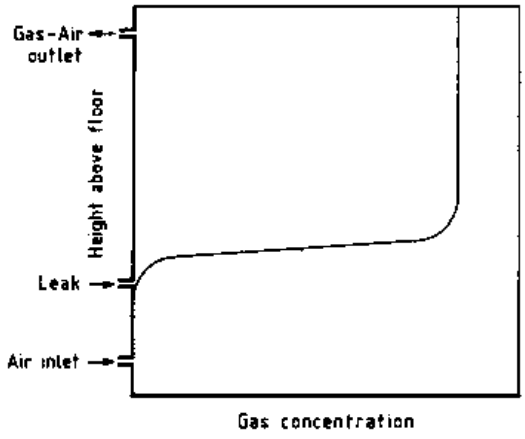

Figure 17.14 *Concentration from a leak of gas lighter than air under conditions of upwards ventilation (after R.J. Harris, 1983) (Courtesy of British Gas)*

A more detailed discussion of ventilation is given in Chapter 10.

17.8.3 Gas accumulation and mixing in buildings

If a leak occurs, the part of the enclosure which is affected depends on the density of the gas, the height of the leak source and the ventilation pattern. The normal ventilation pattern is upward flow. Harris describes experimental work which shows that with this ventilation pattern for a gas with a density lighter than air, such as methane, a high gas concentration tends to build up in the space above the leak source. This situation is illustrated in Figure 17.14.

If the ventilation pattern is downward flow, which is rather unusual, this situation no longer pertains, and high gas concentration can occur below the leak source.

For a gas with a density heavier than air with an upward ventilation pattern the buoyancy and the ventilation act in oppositive directions, and in this case a high concentration will tend to build up in the whole space.

Thus for the normal arrangement of upward flow ventilation the space liable to have a high gas concentration should be taken as the space above the leak for a light gas and as the whole space for other gases.

For practical purposes, the space liable to a high concentration may be assumed to be perfectly mixed, and the gas concentration in the space may be determined from the equation for a single, perfectly mixed stage, which may be written for this case as

$$\tau \frac{dC}{dt} = C_i - C \qquad [17.8.1]$$

with

$$C_i = Q_g/Q \qquad [17.8.2]$$

$$Q = Q_g + Q_a \qquad [17.8.3]$$

$$\tau = V/Q \qquad [17.8.4]$$

where C is the volumetric concentration in the space, C_i is an effective inlet volumetric concentration defined by Equation 17.8.2, Q the total volumetric flow rate, Q_a is the volumetric flow of air, Q_g is the volumetric flow of contaminant gas, t the time, V the volume of the space and τ the volume/throughput ratio, or time constant.

Then for an increase in concentration starting from the time of release

$$\frac{C}{C_i} = 1 - \exp\left(-\frac{t}{\tau}\right) \qquad [17.8.5]$$

and for a decrease in concentration starting from cessation of the release with a concentration C_o at that time

$$\frac{C}{C_o} = \exp\left(-\frac{t}{\tau}\right) \qquad [17.8.6]$$

In this latter case the value of Q to be used in Equation 17.8.3 is $Q = Q_a$, since $Q_g = 0$.

17.8.4 Some structural features of buildings

Much of the work done on explosions in closed containments applies to vessels. There are some significant differences between vessels and buildings.

A building is generally rectangular in shape and the volume enclosed is relatively large. The increase in size and in aspect ratio compared with a vessel can create difficulties in scaling up correlations developed for small compact vessels. Moreover, phenomena which are relatively insignificant on the smaller scale can become important on the larger one.

The space in a building tends to contain obstructions. There are usually multiple compartments which are connected to each other. The presence of obstacles will tend to increase turbulence. So also will the existence of multiple compartments, since gas flowing through open internal doorways will generate turbulence.

The building itself is generally not very strong. An explosion pressure of 7 kN/m^2 (1 psi) is often quoted as that at which a typical brick building may be destroyed. On the other hand, a normal building will have walls which contain weaker members which will fail and in so doing provide vents so that the explosion pressure does not rise as high as it otherwise would.

The static pressures at which certain building components fail has been given by Rasbash (1969c) and by Astbury *et al.* (1970) and are quoted by Lunn (1984b). Some typical values are:

	Failure pressure (kN/m^2)
Windows (normal)	3–4.6
Windows (strained)	1, or even 0.2
Chipboard (19 mm)	7
Brick wall (114 mm)	Survived at 23, destroyed at 35
Brick wall (228 mm)	Survived at 70, destroyed at 105

It has been suggested by Buckland (1980) that the explosion pressure should not exceed 21 kN/m^2 if the building is to avoid serious damage.

Another relevant feature is the natural period of the building. Rasbash (1969c) quotes a value of 40 ms as a typical natural period for the slabs and floors of a

building. W.B. Howard and Karabinis (1980) give further details of natural periods.

Structural damage to buildings from explosions is considered in more detail in Section 17.32.

17.8.5 Gas explosions in buildings

Some features of gas explosions in buildings have been discussed by Rasbash (1969c). The maximum unvented pressure created in an unvented building by the explosion of the most explosive gas mixture is of the order of 7 bar. A 30 m^3 room requires about 2.5 kg of fuel to give such a mixture. The energy of this fuel is equivalent to some 20 kg of TNT.

The pressure from such an explosion will build up relatively gradually, giving a duration of several hundred milliseconds compared with about 1 ms for a condensed phase explosion. Rasbash quotes for a vented explosion with low turbulence a typical duration of 300 ms. But he also gives for the explosion of the most explosive mixture of town gas with high turbulence a duration in the range 20–150 ms.

An account of experimental work on venting of gas explosions in buildings has been given by W.B. Howard and Karabinis (1980, 1982). They state that the durations of the explosions were in the range 40–150 ms. Experimental pressure–time profiles showed that the pressure impulse is well approximated by a triangle with equal rise and decay times.

17.8.6 Modelling of gas explosions in buildings

The pressure in deflagrations in a closed system was considered in Section 17.7. The treatment given there is applicable in broad outline to an explosion in a building, but, as indicated above, there are some important differences. The model of R.J. Harris (1983) described in that section is for explosion in a building, and gives the pressure and rate of pressure rise during the initial stages of the explosion.

Most of the models available for explosions in buildings are for vented explosions. These are considered in Section 17.14. One of these is the model of Runes (1971, 1972). The Runes equation is intended for the design of explosion relief for a building. It has been used, however, by W.B. Howard (1972) to estimate the explosion effects in an explosion incident in a building with open vents.

17.8.7 Condensed phase explosions in buildings

Experiments in which TNT charges were detonated inside a chamber have been described by Weibull (1968). The work was done to develop a nuclear blast simulator in which it would be possible to obtain arbitrary values of peak pressure and duration of the blast wave. The chambers used were provided with a variable vent opening.

Weibull states that in this system the peak pressure would be determined mainly by the mass of the explosive and the duration mainly by the area of the vent opening.

The pressure measured showed several very high initial spikes of very short duration which were reckoned to have minimal effect on the heavy walls of the chamber. The pressure, which had a long duration relative to the period of the walls, was taken as the blast load acting on them. The area of the vent opening had insignificant effect on the smoothed peak pressure. This pressure was given by the equation

$$p = K(Q/V)^a \qquad [17.8.7]$$

where p is the peak pressure (bar), Q is the mass of explosive (kg), V is the volume of the chamber (m^3), K is a constant and a is an index. The value of K is 22.5 and that of a is 0.72.

Further information on pressures in enclosures estimated as a function of a TNT equivalent charge is given in Section 17.26 in the context of design of barriers.

17.9 Explosions in Large Enclosures

The type of large enclosure which is envisaged here is exemplified by an offshore module. It is with such enclosures that the account given in this section is primarily concerned.

An offshore module tends to have a high aspect, or length/diameter, ratio and to contain a number of obstructions in the form of equipment and pipework.

The overpressure generated in the combustion of a vapour cloud is due to two effects. One contribution to the overpressure comes from the production of a large quantity of hot burned gas, the volume production. The other is due to the effect of the flame speed. The overpressure which might occur due to the volume production would be up to about 8 bar, whereas the overpressure due to the flame speed effect might have any value up to that associated with a detonation.

Much work has been done on the development of explosion overpressures in vapour clouds. This work has shown that in the part of the cloud which is free of obstacles the flame speed is relatively low. If the flame passes first through a region which is unobstructed, then through one which is obstructed and finally through one which is unobstructed, the flame accelerates on entering the obstructed region and decelerates on leaving it. The flame speed in the obstructed space can reach quite high values.

17.9.1 Experimental studies

Work on the generation of overpressures in vapour clouds has been done primarily in connection with the explosion of vapour clouds in the open. This work is described in Section 17.28. Most accounts of explosion in semi-confined spaces derive from, or are closed related to, this work.

An account of the experiments to determine the overpressures which might be generated in an offshore module was given by Vasey (1989) in evidence to the Piper Alpha Inquiry. The experimental rig used consisted of an enclosure 46.5 m long, 5 m wide and 4 m high with one end consisting of a confined section, a long box, with an open end, and then an open section, a gallery enclosed only by transparent polyethylene sheet to contain the gas mixture. Obstacle array supports were located every 1.5 m along both the confined and open sections. The obstacles consisted of 3 m lengths of 0.18 m pipes or 0.18 m wide planks. The flame speed was sufficiently high that venting to the side through the sheet did not occur and high overpressures were attained.

Work was done using both natural gas–air and propane–air mixtures. With a natural gas mixture a flame speed of 500 m/s was obtained and the overpressure was several bar. With a propane mixture the flame accelerated to detonation, and the overpressure, both measured and calculated, was about 18 bar.

17.9.2 Simulation models

Several models have been developed to simulate the development of an explosion in a semi-confined space such as an offshore module.

The FLACS model of the Christian Michelsen Institute (CMI) is a computational fluid dynamics (CFD) model which solves the fundamental equations of fluid flow taking account of turbulence and combustion. The three-dimensional Navier–Stokes equations, suitably amplified to include the effects of turbulence and combustion, are cast in discrete form, employing a finite volume technique, and are solved implicitly. Turbulence is modelled in terms of eddy viscosity, and combustion in terms of turbulent, mixing-limited reaction. The space modelled is divided into a grid of 'boxes' of volume 1 m^3. Normal assumptions are that the flammable gas cloud is a quiescent homogeneous stoichiometric mixture so that the effects of any concentration differences within the gas cloud, of any ventilation air flow or of a continuing leak source are neglected. Ignition is modelled as a weak ignition source by assuming that at time zero half of the flammable mixture in one of the boxes has undergone combustion so that the temperature of the gas in the box is correspondingly increased. Accounts of the model have been given by Hjertager (1982a) and by Bakke, Bjerkevedt and Bjorkhaug (1990).

The CLICHE model of British Gas is based on a spherical flame front. It was originally intended for use in simulating explosions in vessels with a high degree of confinement and low flame speeds, but has been extended to allow simulation of different geometries and flow conditions. It has been used to investigate flame acceleration through obstacles and the generation of overpressures much higher than those for which it was originally intended. An account of the model has been given by Catlin (1990).

CFD modelling is discussed further in Section 17.28 in relation to vapour cloud explosions.

17.9.3 Computer codes

There are several computer codes based on simulation models of the type just described.

These codes include FLACS at the CMI (Bakke, Bjerkevedt and Bjorkhaug, 1990), EXSIM (Hjertager *et al.*, 1994), CLICHE at British Gas (Catlin, 1990) and, at the TNO, BLAST (van den Berg, 1980) and REAGAS (van de Berg, 1989).

The FLACS suite of codes comprises a front end program CASD which captures details of the structure of the module and the equipment in it, a program which processes this information into a form in which it can be utilized by the main program, the FLACS code proper.

The FLACS code has been validated by comparison of the results of code simulations with measurements made on experiments on explosions in scale models of modules with 1:33 and 1:5 scale. The overpressures predicted by the code lie within ±30% of those in the model experiments with perhaps 1 case in 20 lying outside this range, corresponding to a confidence level of some 95%. The variability of the model experiments themselves is of the same order.

The FLACS code was used at the Piper Alpha Inquiry to investigate the overpressures which would have resulted from an explosion in one of the modules, as described in Appendix 19. Results from CLICHE were also given in evidence.

Plate 28 illustrates typical output from the FLACS code, showing the contours of the unburnt fuel, the burnt combustion products and the overpressures and the wind velocity vectors.

17.10 Explosion Prevention

Prevention of gas and vapour explosions in general depends on (1) avoidance of flammable mixtures and (2) elimination of sources of ignition. These general requirements for explosion prevention have already been discussed.

For plant, or closed, systems an important method of eliminating flammable mixtures which merits further consideration is (3) atmosphere control. This is therefore discussed below.

Other aspects of explosion prevention which have already been discussed earlier include avoidance of runaway chemical reactions and of excessive fluid pressures.

Selected references on explosion prevention, protection and relief are given in Table 17.13.

17.10.1 Atmosphere control

The hazard of explosion can be much reduced by control of the atmosphere to render it non-flammable. This control is often effected by the use of an inert gas.

The atmosphere control of process plant has been discussed by Craven (1975). An account of inerting in tankers has been given by Halvorsen (1975).

In general, the use of atmosphere control is a much more reliable method than the elimination of sources of ignition, which is very difficult to achieve. Craven comments:

> The elimination of ignition sources is often promoted as an alternative to atmosphere control to prevent explosions. There are few situations in the process industries today in which this philosophy can be seriously defended.
>
> Only in the simplest situations – such as isolated liquid storage – can the elimination of ignition sources seriously compete with atmosphere control as the first line of defence.

For an atmosphere which may contain flammable gas, air and inert gas, Craven distinguishes four regions. These are:

Region I	Flammable mixture
Region II	Fuel-lean mixture
Region III	Oxygen-deficient mixture
Region IV	Fuel-rich mixture

The atmosphere is non-flammable in all but the first of these regions. Atmosphere control is often effected by the use of inert gas, but this is not the only option. In

Table 17.13 *Selected references on explosion prevention, protection and relief*

SMRE (Explosion 4); J.H.F. Smith (1956): Maisey (1957); Ghormley (1958); Burgoyne (1961); Grabowski (1964); Adcock and Weldon (1967a); Charney (1967); Allan and Athens (1968); Bartknecht (1968, 1974a, 1981a); Callahan (1968); E. Cohen (1968); Jarrett (1968); Constance (1971b); Conrad (1973); Donat (1977b); Grein (1973); K.N. Palmer (1973a); Franke *et al.* (1975); Funke (1976); R.L. Allen (1977a); Carver *et al.* (1977); Glatt (1977); Rogowski (1977); Schampel and Steen (1977); Ray (1978); P.E. Moore (1982a,b, 1990); IBC (1983/41, 1984/47, 49 Pt 1); Haessler (1986); Huff (1988); Nazario (1988); I. Swift (1988c); FPA (1989 CFSD FS 6012); Haverstad (1989); Tuhtar (1989); Vodyanik (1990); NFPA (1992 NFPA 69, 1994 NFPA 68)
CCPS Guidelines: Huff (1992)

Flame arresters
FRS (n.d., Fire Res. Note 1037, 1967 Fire Res. Note 658, 1972 Fire Res. Notes 931, 945, 1973 Fire Res. Notes 964, 974); Radier (1939); Egerton, Everett and Moore (1953); Cubbage (1959, 1963); K.N. Palmer (1959, 1960); Joint Fire Research Organization (1960); Quinton (1962); K.N. Palmer and Tonkin (1963); HSE (1965 HSW Bklt 34); Litchfield (1965); K.N. Palmer and Rogowski (1967); Leineman (1970); H. Phillips (1972b); J.P. Davies, Palmer and Rogowski (1973); Barton, Carver and Roberts (1974); W.B. Howard, Rodehorst and Small (1975); Rogowski (1975, 1980); BRE (1978/8); R.P. Wilson and Flessner (1979); Worrell (1979); Amal Ltd (1980); Borger *et al.* (1980); HSE (1980 HS(G) 11); Peter (1980); Anon. (1981 LPB 41, p. 13); Bjorklund, Kshida and Flessner (1982); W.B. Howard (1982, 1988 LPB 79, 1992a,b); Kletz (1982c); Thorne (1982); Broschka *et al.* (1983); O.W. Johnson (1983); Lietze (1983); IMC (1984); UL (1984 UL 525); Lunn and Przybylski (1985); H. Phillips and Pritchard (1986); Wilkie (1987b); Fellensiek *et al.* (1987); Stalder (1987); Watson (1988 LPB 79); Overhoff *et al.* (1989); Babkin, Korzhavin and Bunev (1991); Piotrowski (1991); Roussakis and Lapp (1991); Capp (1992, 1994); S.P. Cooper *et al.* (1992); Rubach, Schecker and Onken (1992); Bishop and Knittel (1993); Mendoza, Smolensky and Straitz (1993); Siwek and Wegmuller (1993); G.O. Thomas and Oakley (1993)
BS 7244: 1990

Explosion protection
Grabowski (1958, 1968); Rentsch (1971); Yasuhara, Kita and Hiki (1978); Woods and Speechly (1979); Maisey (1980); J.M. Wilson and Tyrer (1980); Kirby (1985a); Altorfer (1992); Cadeddu *et al.* (1992); S.P. Cooper and Moore (1993); BS (Appendix 27 *Explosion Protection*)
Pipes: HSE (1965 HSW Bklt 34); Flessner and Bjorklund (1980, 1981); Bartknecht (1981a); O.W. Johnson (1983); Steen and Schampel (1983); Chatrathi (1992b,c)
Buildings: K.N. Palmer and Tonkin (1980); C.J.M. van Wingerden and Zeeuwen (1983); Mercx, van Wingerden and Pasman (1992)
Jetties: Dicker and Ramsey (1983)

Design against explosion
Grein (1973); Guill (1973)

Explosion containment
Bartknecht (1981a); Donat (1982); Noronha, Merry and Reid (1982); Kirby (1985a); Kirby and Siwek (1986); Wilday (1991)

Explosion prevention by inerting
Penland (1967); Kletz (1971); Craven (1975); Halvorsen (1975); O'Shea (1983); Blakey and Orlando (1984)

Explosion isolation
Chatrathi (1991); Chatrathi and Degood (1991)

Explosion suppression
Merewood (1958); Lafitte and Boucher (1959); Hammond (1961); Grabowski (1964, 1965); Graviner (Colnbrook) Ltd (1966); Charney and Lawler (1967); Charney (1969); FPA (1974 CFSD FS 6015); P.E. Moore (1979b, 1981, 1982b, 1984, 1986, 1990); J. Singh (1979c); Maisey (1980); S.R. Moore and Weinberg (1981); Westbrook (1982c); Hertzberg *et al.* (1985); P.E. Moore and Bartknecht (1986); P.E. Moore and Cooper (1993)

Explosion suppression in modules, including water sprays
G.O. Thomas, Edwards and Edwards (1990); G.O. Thomas, Jones and Edwards (1991); A. Jones and Thomas (1992, 1993); Catlin *et al.* (1993)

Explosion venting
G.W. Jones, Harris and Beattie (1933 BM Tech. Pap. 553); Bonyun (1935, 1945); Creech (1941); Murphy (1944a,b); H. Brown (1946); Coffee, Raymond and Crouch (1950); Benson and Burgoyne (1951); Cousins and Cotton (1951a,b); Cubbage and Simmonds (1955a–c, 1957a–c); Gas Council (1955 GC 23, 1957 GC 43); Schmidt, Haberle and Recklinghausen (1955); FRS (1956 Fire Res. Note 248); Burgoyne and Wilson (1957, 1960); Grumer, Cook and Kubala (1959); Rasbash and Rogowski (1960a,b); Simmonds and Cubbage (1960); Spalding (1960); Westenberg and Favin (1960); D.S. Davis (1961); Raezer (1961); Spalding and Jain (1961); Spalding, Jain and Samain (1961); Block (1962); Munday (1963, 1974); Philpott (1963); Rogowski and Rasbash (1963); Salter, Fike and Hansen (1963); W.H. Doyle (1964); Pliickenbaum, Strauss and Edse (1964); Maisey (1965); Heinrich (1966, 1974); Charney (1967); Grein and Donat (1967); G.F.P. Harris (1967); G.F.P. Harris and Briscoe (1967); Woods and Thornton (1967); Bartknecht (1968, 1972b, 1974a, 1975, 1977a, 1981a); FMRC (1969/1, 1973/2); Yao *et al.* (1969); Walker (1970); Decker (1971); R.L. Miller and Howard (1971); Donat (1971a,b, 1973a–c, 1977a,b); Cubbage and Marshall (1973, 1974); Institution of Gas Engineers (1973 Comm. 926); W.W. Russell (1973); Butlin and Tonkin (1974 FRS Fire Res. Note 1019); W.B. Howard and Russell (1974); Yao (1974, 1982); Nettleton (1975, 1978b); D. Bradley and Mitcheson (1976, 1978); Guirao, Bach and Lee (1976); Sapko, Furno and Kuchta (1976 BM RI 8176); Anthony (1977b, 1977–78); Chappell (1977); Fiumara (1977); N. Gibson (1977); Hattwig (1977); M.R. Marshall (1977); V.M. Morton and Nettleton (1977); Crescitelli, Russo and Tufano (1979a, 1980); J.G. Marshall (1979); Monk and Davis (1979); Rust (1979); J. Singh (1979b, 1984, 1988a,b, 1989); D.K. Burchett (1980); Hattwig (1980); HSE (1980 HS(G) 11); Solberg, Skramstad and Pappas (1980);

Zalosh (1980b, 1982); Solberg, Pappas and Skramstad (1981); Tufano, Crescitelli and Russo (1981); Fairweather and Vasey (1982); Hirano (1982, 1984); J.H.S. Lee and Guirao (1982b); Noronha, Merry and Reid (1982); Porter (1982); Fearnley and Nettleton (1983); J.H.S. Lee (1983a); I. Swift (1983, 1984, 1988a,b, 1989); Thorne, Rogowski and Field (1983); Chippett (1984); Cummings *et al.* (1984); Eckhoff *et al.* (1984); Llewellyn (1984); Hart (1985); McCann, Thomas and Edwards (1985); Champion *et al.* (1986); M.G. Cooper, Fairweather and Tite (1986); Degood (1986); M. Epstein, Swift and Fauske (1986); D.J.Lewis (1986a); Seifert and Giesbrecht (1986); Simpson (1986); Starke and Roth (1986, 1989); I. Swift, Batz and Degoode (1986); Schwab (1987); I. Swift and Epstein (1987); de Groot and Heemskerk (1989); Kumar, Dewit and Greig (1989); M. Epstein *et al.* (1990); Itagaki, Miyake and Ogawea (1990); Phylaktou, Andrews and Herath (1990); W.E. Baker, White and Hokanson (1991); Cates and Samuels (1991); Degood and Chatrathi (1991); Makhviladze and Phillipov (1991); Rota *et al.* (1991); Santon *et al.* (1991); Chathrathi (1992a); K. Bell and Morris (1992); Chaineaux and Danin (1992); Haaverstad (1992); Mercx, van Wingerden and Pasman (1992, 1993): Parry (1992); Rota *et al.* (1992); Skouloudis (1992); Wu and Swithenbank (1992); Anon. (1994a); Scheuermann (1994); NFPA (1994 NFPA 68).

Module venting: Committee for Explosion Research (1958); Hirano (1982); Hjertager (1982a); Moen (1982a); Solberg (1982a); P.F. Thorne (1982)

Effects in outside vent system, acoustic coupling and instabilities: Wiekema, Pasman and Groothuizen (1977); K.N. Palmer and Tonkin (1980); Zeeuwen (1982); Kordylewski and Wach (1986, 1988); A.J. Harrison and Eyre (1987b); I. Swift (1988c); C.J.M. van Wingerden and Zeeuwen (1988); Frolov, Gelfand and Tsyganov (1990); Tamanini and Chaffee (1992a,b); Ural (1993)

Reactor venting

Tangren, Dodge and Seifert (1949); Gasche (1956); Block (1962); Sestak (1965); Boyle (1967); Harmon and Martin (1970); Schlegel (1972); W.B. Howard (1973); Huff (1973, 1977a,b, 1982a,b, 1984a,b, 1985, 1987, 1988, 1990, 1992); Duxbury (1976, 1979a,b, 1980); W.E. Baker, Esparza and Kulesz (1977); Kneale and Binns (1977); Gartner, Giesbrecht and Leuckel (1978, 1980); BPF (1979); IChemE (1979/117); Karmarkar (1979); V.C. Marshall and Cockram (1979); Minors (1979); J. Singh (1979a, 1988a, 1989, 1990a,b, 1992a); Townsend and Pantony (1979); Booth *et al.* (1980); Fauske *et al.* (1980); de Groot, Groothuizen and Verhoeff (1980); Mejdell (1980); Mayinger (1981); Friedel and Löhr (1982); Solberg, Pappas and Skramstad (1982); Friedel and Purps (1983, 1984a,b); Steen and Schample (1983); Barton and Nolan (1984); Binns and Barrett (1984); Harmon and Stuper (1984); Quinn, Weir and Hoppe (1984); P.W. Thomas (1984); I. Swift (1985); Giesbrecht and Seifert (1986); Schulz and Schoft (1986); Duxbury and Wilday (1987, 1989, 1990); Friedel and Kissner (1988); Nolan and Proctor (1988); First and Huff (1989); D.P. Mason (1989); Tharmalingam (1989a); Wilday (1989, 1989 LPB 89); Banerjee, Prandini and Patroncini (1990); Gustin (1990); Oster, Bell and Koltowski (1990); Sumapathala, Venart and Steward (1990a,b); H.G. Fisher (1991); Skouloudis and Kottowski (1991); K. Bell, Morris and Oster (1993); Friedel and Schmidt (1993); Duffield and Nijsing (1994); Goetz and Sawrey (1994); Snee and Hare (1994); Waldram (1994).

Particular reactions: Crowley and Block (1989); J. Singh (1992a, 1994); Gustin *et al.* (1993); Whitmore, Cutler and Gladwell (1994); Yue, Sharkey and Leung (1994)

Reactor venting: DIERS

Fauske, Grolmes and Henry (1983); I. Swift, Fauske and Grolmes (1983); Fauske (1983, 1984a–c, 1985a, 1987a,b, 1988a, 1989a, 1990); I. Swift (1984); Anon. (1985g); Fauske, Grolmes and Leung (1984); Fauske and Leung (1985); H.G. Fisher (1985, 1986, 1989, 1991); Grolmes and Leung (1985); Grolmes, Leung and Fauske (1985, 1989); Klein (1986); Leung (1986b, 1987, 1992b); Leung, Fauske and Fisher (1986); Noronha (1986); N. Gibson, Maddison and Rogers (1987); Leung and Fauske (1987); Wilday (1987); Leung and Epstein (1988); J. Singh (1988a); M. Epstein, Fauske and Hauser (1989); Fauske, Clare and Creed (1989); Fauske, Grolmes and Clare (1989); Gustin (1989b); Leung, Creed and Fisher (1989); Leung and Fisher (1989); Leung, Stepaniak and Cantrell (1989); Noronha, Seyler and Torres (1989); Skouloudis *et al.* (1989); Creed and Fauske (1990); M. Epstein *et al.* (1990); Kirch, Magee and Stuper (1990); Skouloudis, Bell and Kotowski (1990); Friedel and Wehmeier (1991); Grossel (1991); DIERS (1992); Prugh (1992d); C.M. Sheppard (1992, 1993, 1994); Grolmes and Yue (1993)

Reaction forces

Faber (1982); Porter (1982); Beveridge (1984); Huff (1990); Parry (1992)

Disposal of vented material

Kneale (1984, 1989); Faukse (1986a, 1990, 1992); Grossel (1986, 1990b); Muschelknautz and Mayinger (1986, 1990); Keiter (1989, 1992); Fauske and Grolmes (1992); Friedel, Schmidt and Wehmeier (1992); Hermann, Schecker and Schoft (1992); Parry (1992); Rupert, Muschelknautz and Klug (1992); J. Singh (1992b); Spatz, Drees and Schoft (1992); Lindsay and Rogers (1994)

Building venting

FRS (Fire Res. Note 820, 1969 Fire Res. Note 759, 760, 1975 Fire Res. Note 1026); Rasbash (1969c); Astbury *et al.* (1970); Mainstone (1971); Runes (1971, 1972); Astbury, West and Hodgkinson (1972, 1973); Dragosavic (1972a,b, 1973); W.B. Howard (1972, 1980); Butlin (1975 FRS Fire Res. Note 1026); Naidus (1976, 1981a,b); Rasbash, Drysdale and Kemp (1976); Anthony (1977/78); W.B. Howard and Karabinis (1980, 1982); Cummings *et al.* (1984); NFPA (1994 NFPA 68)

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some cases it is more appropriate to operate in the fuel-rich region.

Some operations and equipments in which atmosphere control is practised are (1) reactors, (2) storage tanks, (3) head tanks, (4) centrifuges, (5) driers and (6) pneumatic conveyors.

Generally in an oxidation reactor the off-gas is deficient in oxygen. The oxygen concentration is usually analysed, and action is taken if it rises. This action may

be to shut off an air or oxygen feed to the reactor or to inject inert gases.

Such trip systems are required to act very rapidly, and time delays can be a problem. There may also be difficulties in gas sampling due to vapour drops or solid particles. In some cases, therefore, other measurements, such as reactor temperature, may be used to complement the oxygen measurement by giving advanced warning of abnormal conditions.

Storage tanks containing flammable liquids are often blanketed with inert gas. The quantity of inert gas required can be large due to the movements of the liquid surface. An economical system is the use of breather vacuum valves which admit inert gas only when the liquid level falls.

The effectiveness of inerting in reducing the probability of storage tank fire/explosion has been discussed by Kletz (1971).

Inert gas blanketing is also frequently provided in constant head tanks for flammable liquids. Difficulties are often experienced, however, in maintaining an inert atmosphere in a head tank fitted with an overflow, because the return pipe from the overflow tank tends to act an air entrainment pump. This problem can be eliminated by fitting suitable gas balance lines.

An inert atmosphere is necessary in centrifuges handling flammable liquids as described in Chapter 11. Again the consumption of inert gas may be high due to air ingress during operation, but the use of gas balance lines can effect appreciable reductions.

The provision of inert atmospheres in dust-handling plant is considered in Section 17.46.

The quantity of inert gas used must not be excessive if inerting is to be economic. It is important, therefore, to seek to minimize inert gas consumption.

For a perfectly mixed system the concentration changes effected by a ventilating air or purge gas flow are given by the equation

$$\frac{c}{c_o} = \exp\left(-\frac{Qt}{V}\right) \qquad [17.10.1]$$

where c is the volumetric concentration of the component in the system atmosphere, Q is the volumetric flow of gas through the vessel, t is the time, V is the volume of the vessel, and the subscript o denotes the initial value.

Equation 17.10.1 may be rewritten as

$$\log_{10}\left(\frac{c}{c_o}\right) = -\frac{E}{2.3} \qquad [17.10.2]$$

with

$$E = Qt/V \qquad [17.10.3]$$

where E is the number of changes of atmosphere. Thus the concentration of a component in the system atmosphere can be reduced by a factor of 10 by 2.3 changes and by a factor of 100 by 4.6 changes.

Purging can be effected more economically, however, if the flow regime is plug flow rather than perfect mixing. Plug flow can often be achieved if the vessel is one with a very high aspect ratio, such as a tall column or a pipeline. Other situations which allow plug flow are buoyant displacement with a cold gas and gravitational displacement of a heavy vapour.

If the density difference between the atmosphere to be purged and the purge gas is small, it is necessary to achieve turbulent mixing. For a simple vessel such as a storage tank without baffles, Craven states that such mixing should be obtained by the use of gas jets directed across the tank with final velocities in the remote corners of 300 ft/min. He gives the following equation for the nozzle velocity required to give an air velocity of 300 ft/min along the jet axis in the remote corners

$$\frac{V_o}{V_x} = \frac{1}{K}\frac{X}{D} \qquad [17.10.4]$$

where D is the diameter of the jet orifice (ft), V_o is the nozzle velocity (ft/min), V_x is the required velocity (ft/min) (=300), X is the distance from the jet to the most remote corner (ft) and K a constant (=6).

17.11 Explosion Protection

Explosion protection and relief include the following aspects:

(1) containment;
(2) separation;
(3) flame arresters;
(4) automatic isolation;
(5) automatic explosion suppression;
(6) explosion venting of vessels;
(7) explosion venting of pipes and ducts;
(8) explosion relief of buildings;
(9) explosion relief of large enclosures;
(10) venting of chemical reactors.

Deflagration and detonation inside plants has been discussed in Sections 17.5 and 17.6, and explosion in closed vessels specifically in Section 17.7.

Protection by containment of the explosion is a potential design option, but as discussed in Section 17.5, it is usually not practicable except for small-scale plant.

Another method of containment is the use of blast walls and barricades, and of blast cubicles. The design of such blast protection is described in the *High Pressure Safety Code* (B.G. Cox and Saville, 1975) and by W.G. High (1967) and Callahan (1968).

Separation as a method of protection is discussed in relation to plant siting and layout in Chapter 10 and in relation to storage in Chapter 22. It is also considered in Section 17.3 in terms of the quantity–distance relations used for storage of explosives.

Methods of explosion protection and relief are described in *Dust Explosions and Fires* (K.N. Palmer, 1973a) and *Explosions* (Bartknecht, 1981a). Health and Safety Executive (HSE) guidance is given in *Guide to the Use of Flame Arresters and Explosion Reliefs* (the HSE *Explosion Relief Guide*) (1965 HSW Bklt 34). Relevant US codes are NFPA 69: 1992 *Explosion Prevention Systems* and NFPA 68: 1994 *Deflagration Venting*.

Selected references on explosion prevention, protection and relief are given in Table 17.13.

17.11.1 Flame arresters

A flame arrester, or flame trap, is a device used to prevent the passage of a flame along a pipe or duct.

Accounts of flame arresters include those given in the HSE *Explosion Relief Guide* (1965 HSW Bklt 34) and by H. Phillips (1972b), Barton, Carver and Roberts (1974), W.B. Howard, Rodehorst and Small (1975), W.B. Howard (1982, 1992a,b), Kletz (1982c), Thorne (1982), Lunn and Przybylski (1985), H. Phillips and Pritchard (1986), Capp (1992, 1994) and G.O. Thomas and Oakley (1993).

An extensive programme of work on flame arresters was conducted in the 1960s by the Joint Fire Research Organization (JFRO) at the Fire Research Station at Borehamwood. Accounts of this work have been given by K.N. Palmer and co-workers (e.g. K.N. Palmer and Tonkin, 1963; K.N. Palmer and Rogowski, 1967; J.P. Davies, Palmer and Rogowski, 1973; Rogowski, 1980).

The UK has had certain long-standing but limited legal requirements for the use of flame arresters, on diesel engines in mines and on equipment using acetylene above 0.62 barg. Their use is recommended in codes.

A flame arrester is generally an assembly of narrow passages through which gas or vapour can flow, but which are too small to allow the passage of flame.

Typical applications of flame arresters are on vents of storage tanks containing flammable liquids, on pipe systems supplying fuel gas to burners, on certain pipelines conveying flammable gases within the plant and on flare stacks. Flame arresters are also used on exhausts of engines working in atmospheres with a flammability hazard and on crankcases of small engines.

Flame arresters are generally distinguished as end-of-line or in-line arresters.

17.11.2 Flame arresters: modes of combustion

In general, combustion may take the form of a deflagration or a detonation. The characteristics of these two forms of combustion have been described above.

In the context of flame arresters, W.B. Howard (1992a) characterizes a deflagration as having a flame speed of 3–60 m/s and generating a pressure of 8–11 bara, with the corresponding values for a detonation being 2000 m/s and 20–100+ bara, respectively.

An end-of-line arrester is designed to prevent the passage of a deflagration from the downstream to the upstream side.

An in-line arrester should be able to stop either a deflagration or a detonation passing in either direction. Although it is often assumed that detonation presents the more difficult duty, this is not necessarily so. Some detonations are overdriven, and if this is a possibility the arrester needs to be able to handle this form of detonation.

Definition of the nature of the flame with which an arrester may have to cope is difficult, so that in principle it may be necessary to allow for both deflagration and detonation, possibly including overdriven detonation.

It should be appreciated that even if a flame arrester prevents the passage of the detonation flame, it does not stop the detonation shock wave.

17.11.3 Flame arresters: types of arrester

The types of flame arrester used are described in the HSE *Guide* and FPA FS 6012 and by H. Phillips and Pritchard (1986) and W.B. Howard (1992a).

Howard defines three types of arrester:

Type 1	Arresters with multiple small channels
Type 2	Hydraulic devices
Type 3	Velocity flame stoppers

Some principal type 1 flame arresters are

(1) sheet metal arresters –
  (a) planar sheet metal arresters,
  (b) cylindrical sheet-metal arresters (crimped ribbon arresters);
(2) perforated plate arresters;
(3) perforated block arresters;
(4) sintered arresters;
(5) expanded metal arresters;
(6) parallel plate arresters;
(7) wire gauze arresters;
(8) wire pack arresters;
(9) packed bed arresters.

Figure 17.15 illustrates some of these types of arrester.

The operation of a type 1 arrester is generally treated in terms of the mechanism of quenching and of heat loss. These are a large part of the story, but not the whole, as discussed by H. Phillips and Pritchard (1986).

Desirable properties of a flame arrester are high free cross-sectional area available for flow, low resistance to flow and freedom from blockage; a high capacity to absorb the heat of the flame; and the ability to withstand mechanical shock, including explosion.

Sheet metal arresters are of two main types. The planar type consists of thin, planar sheets with corrugations or protuberances stacked in a block. The cylindrical type is constructed by winding a thin corrugated metal ribbon to form a cylindrical assembly. This type is also known as a crimped ribbon arrester.

Crimped ribbon arresters are an important type of arrester and are available in a range of designs. These arresters have about 80% free cross-sectional area, can be manufactured to close tolerances, are robust enough to withstand mechanical and thermal shock, and can be made to quench violent explosions.

Wire gauze arresters have a lower free area, which with fine gauzes is less than 50%. They also tend to be less effective and less robust. They have a limited ability to quench flame and are not suitable for violent explosions. A limited enhancement of arrester effectiveness can be obtained by using a number of wire gauze arresters in series as a combined pack.

Perforated plate arresters have a lower free area than gauzes, but higher heat capacity and greater mechanical robustness than wire gauzes, but they are little more effective and again are not suitable for violent explosions.

Perforated metal blocks can also be used as arresters.

Sintered arresters again have a low free area and high flow resistance. Their main use is on flammable gas detectors and on welding equipment.

Parallel, or stacked, plate arresters have a low free area and high flow resistance, but can be designed to quench violent explosions. They are used particularly on the exhausts of internal combustion engines.

Wire pack arresters are made by compressing a pack of wire which has been knitted or assembled at random. This type of arrester tends not to have very reproducible characteristics.

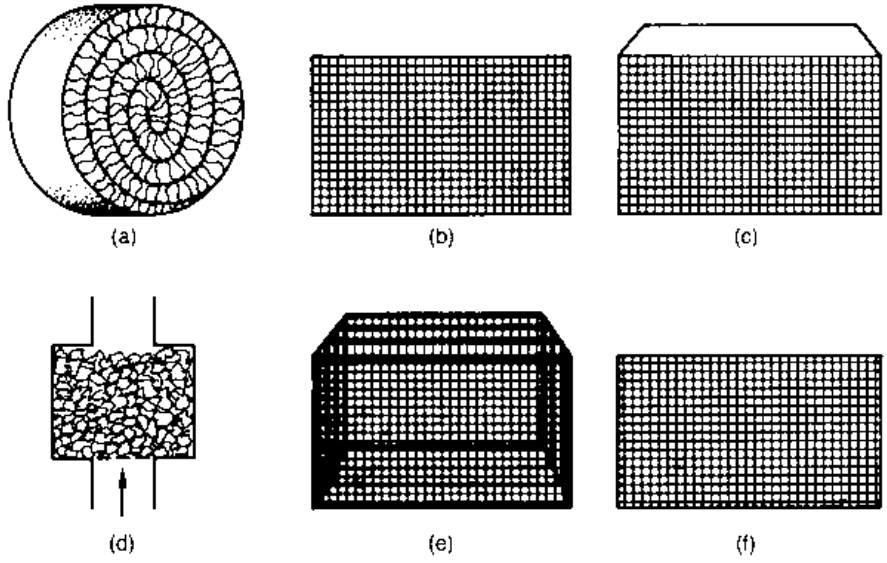

Figure 17.15 *Some types of flame arrester (after Fire Protection Association, 1989 FS 6012): (a) crimpled ribbon arrester; (b) perforated metal sheet; (c) perforated metal block; (d) box of pebbles or ceramic rings; (e) wire gauzes in series; (f) construction of a gauze arrester*

Packed bed arresters are vertical containers fitted with pebbles, Raschig or Pall rings or similar packings. The packing may be irrigated with water or oil. The size of the passages is not well defined. This type of arrester has high flow resistance. Such an arrester can quench a violent explosion, but movement of packing due to such an explosion can result in arrester failure. A more detailed account of packed bed arresters is given by W.B. Howard (1992a).

The design of a flame arrester depends on the combustion properties of the flammable mixture and on the function and location of the arrester.

The size of the aperture through the arrester is determined by the quenching distance of the flammable mixture. Quenching distances have been discussed in Chapter 16. The diameter of the aperture of an arrester should be smaller than the quenching diameter by at least 50%.

The performance of an arrester is affected by the temperature. The quenching distance increases as the temperature increases. It is approximately inversely proportional to the square root of the absolute temperature.

In general, such flame arresters are cheap, can be easily installed and are readily replaced if damaged. They do present some problems, however, due to their fine structure. These include high pressure drop and blockage. They are not suitable, therefore, in dusty gases. The maintenance of an arrester is relatively simple, but it is essential that it should not be neglected if the device is to function properly when required.

17.11.4 Flame arresters: hydraulic devices

Hydraulic, or liquid seal, arresters contain a liquid, usually water, which serves to break up the gas stream into bubbles and so prevents passage of the flame. This type of arrester operates on a quite different principle from that of the other types described. The arrester is effective only if the liquid level is maintained and the gas flow is kept within the range in which it is broken into bubbles.

Hydraulic arresters exist which are reported to be effective in preventing flame propagation in both directions. Tests to establish this on a particular arrester design have been described by Flessner and Bjorklund (1981).

A particular kind of hydraulic arrester is the Linde hydraulic valve developed for acetylene duty. This is described by Flessner and Bjorklund (1981).

Hydraulic arresters are discussed further by W.B. Howard (1992a), with comments on the extent to which the various kinds of arrester are in general use.

17.11.5 Flame arresters: velocity flame stoppers

A velocity flame stopper is an arrester used in end-of-line applications. It function is to prevent a flame passing from the downstream to the upstream side.

Its operates on a quite different principle from other types of arrester. This principle is to ensure that the velocity of the upstream gas passing through the arrester is sufficiently high to prevent a flame propagating through the arrester from the downstream side.

The velocity flame stopper is discussed by W.B. Howard (1992a). For the velocity necessary to prevent flashback through apertures larger than those which would give quenching, Howard quotes the equation of Hajek and Ludwig (1960):

$$u_T = 0.2015 g_L D \qquad [17.11.1]$$

where D is the internal diameter of the pipe (m), g_L is the laminar velocity gradient (s^{-1}) and u_T the turbulent flashback velocity (m/s). The parameter g_L is also termed the critical boundary velocity gradient. This parameter is a function of the gas and of its concentration. It tends to have a maximum value at a concentration somewhat above the stoichiometric. The following maximum values are based on the work of Grumer, Harris and Rowe (1956 BM RI 5225):

Gas	*Maximum laminar velocity gradient, g_L* (s^{-1})
Methane	400
Ethane	650
Propane	600
Ethylene	1 500
Propylene	700
Hydrogen	10 000

Howard recommends that for normal design the minimum velocity through the holes of a velocity flame stopper should be four times the turbulent flashback velocity given by Equation 17.11.1.

A velocity flame stopper is effective only as long as there is a sufficient gas flow through it. Ensuring a reliable gas flow may not be a simple matter, and in such cases a regular flame arrester may be a more attractive alternative.

Velocity flame stoppers are used particularly on certain gas flows to furnaces.

17.11.6 Flame arresters: conservation vents

Storage tanks are commonly provided with conservation vents to allow them to 'breathe'. Over the years there has been some debate as to whether it is necessary to incorporate a flame arrester in such a vent. The question is discussed in Chapter 22. The view has emerged that a conservation vent acts, in effect, as a velocity flame stopper and that a separate flame arrester is not necessary.

17.11.7 Flame arresters: critical flame speed

It was shown by Palmer at the Fire Research Station (FRS) that a crucial variable in the performance of flame arresters is the flame velocity incident on the arrester, or critical flame speed.

The critical flame speed is discussed by H. Phillips and Pritchard (1986), drawing largely on the FRS work on propane–air mixtures at atmospheric pressure. A simple model based on heat abstraction from the flame yields the following relation:

$$V = 0.95 \frac{nyp_o}{p} \qquad [17.11.2]$$

where n is the number of apertures per unit area of arrester surface (cm^{-2}), p is the explosion pressure at the arrester, p_o is atmospheric pressure, V is the flame speed at the arrester (m/s) and y is the thickness of the arrester elements (cm). This equation includes the term (p_o/p), which takes into account the explosion pressure. The authors state that for the system considered this equation gave reasonable agreement, with a number of qualifications, including the facts that it applies only to crimped ribbon arresters of a particular design and to propane–air mixtures. They also quote the following empirical equation:

$$V = 0.38 \frac{ay}{d^2} \qquad [17.11.3]$$

where a is the fractional free area of the arrester, d the diameter of the apertures (cm), V is the flame speed at the arrester (m/s) and y is the thickness of the arrester elements (cm). This equation applies to crimped ribbon, wire gauze and perforated plate arresters. For the former, d is taken as the hydraulic mean diameter. The equation does not taken into account the explosion pressure and is therefore limited to applications where the pressure does not rise substantially above atmospheric; the authors instance a short length of straight pipe.

17.11.8 Flame arresters: applications and requirements

The duty which the arrester performs depends on the nature of the system and on the location of the arrester.

One basic distinction is between (1) end-of-line and (2) in-line arresters. The typical application of an end-of-line arrester is on the vent of an atmospheric storage tank. The function of such an arrester is primarily to stop a flame arising from ignition of vapour vented. The flame is thus of low speed and at atmospheric pressure.

In-line arresters are used in plant pipework and the demands placed on them are much more severe and varied. They may have to deal not only with deflagrations but also with detonations.

Some of the differences in application which arise from the location of the arrester and of the ignition source are discussed in the HSE *Guide*, which distinguishes the following three standard situations: (1) ignition at the open end of a duct, (2) ignition at the closed end of a duct and (3) ignition near the arrester. These situations are shown in Figure 17.16.

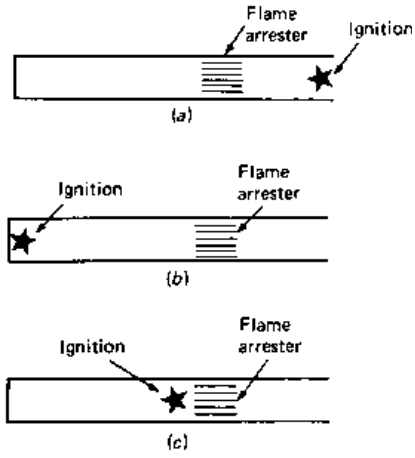

Figure 17.16 *Ignition situations relevant to the design of flame arresters (after Health and Safety Executive, 1965 HSW Bklt 34): (a) ignition at open end of duct; (b) ignition at closed end of duct; (c) ignition near arrester (Courtesy of HM Stationery Office)*

Another relevant distinction is between a stationary and a flowing mixture. Consider first a stationary mixture. If ignition occurs at the open end of the duct, the arrester is required only to quench the flash of flame. If ignition occurs at the closed end of the duct, the arrester must quench the flame and withstand the pressure created by combustion within the duct, but the cooling of the hot gases is effected mainly by the duct walls. If ignition occurs near the arrester, the arrester is required to quench the flame, to withstand the pressure created by the combustion and to absorb the heat from the hot gases.

Now consider a flowing mixture. Assume that in Figure 17.16 the flow is from left to right. If ignition occurs in the open end and the gas velocity is high, the flame may be swept out of the duct or may stabilize on the end of the duct or at a restriction in the duct. In either case the arrester is unaffected. But if the gas velocity is low, the flame will stabilize on the arrester. If ignition occurs at the closed end of the duct or near the arrester, the flame may again stabilize on the arrester.

Thus if a flame arrester is installed in a system in which the gas mixture is flowing, there is a risk of stabilization of the flame and overheating of the arrester. It is necessary, therefore, to arrange for this condition to be detected and for the gas flow to be shut off when it occurs.

The function which a flame arrester is required to perform therefore varies. In some cases it is required only to prevent simple flashback, but in others, where hot gases may be forced through it or where flame may stabilize on or near the arrester, it must also be capable of absorbing a considerable quantity of heat. For the latter duties it is necessary not only that the arrester have apertures smaller than the quenching diameter but also that it have sufficient mass and suitable material of construction to absorb heat.

In many applications a flame may arrive at the arrester from either direction and the arrester needs to be capable of stopping the flame in both cases.

17.11.9 Flame arresters: HSE *Guide*

It is convenient at this juncture to consider the guidance on flame arresters given by the HSE *Explosion Relief Guide*.

This guide is based on the work in the 1950s and 1960 at the FRS, already mentioned. It was, however, the only such guide found in the review of the field in 1986 by Phillips and Pritchard.

The following is a summary of the guidance in this HSE *Guide*. Unless otherwise stated, it applies to gas mixtures at atmospheric pressure.

For crimped metal, wire gauze and perforated plate arresters the following equation is given in the HSE *Guide* for the calculation of the maximum flame speed for a deflagration at atmospheric pressure which can be quenched by an arrester:

$$V = 0.5\frac{ay}{d^2} \qquad [17.11.4]$$

where a is the fractional free area, d is the diameter of the aperture (in.), V is the flame speed (ft/s) and y is the thickness of the arrester (in.).

Equation 17.11.4 is applicable to deflagration but not to detonation. The value of the flame speed V given includes a safety factor which takes account of experimental scatter. For non-circular apertures the equivalent hydraulic diameter should be used.

For crimped metal arresters, the equivalent diameter for a right angle isosceles triangle is 0.83 $\times$ crimp height. The thickness of a crimped metal arrester should be at least 0.5 in.

For a wire gauze arrester, Equation 17.11.4 applies only to a single layer of gauze. For a single layer of gauze the thickness y is twice the wire diameter.

An increase in flame speed of about 20% of the original value may be obtained for each additional layer up to a maximum of five, but further increase gives no additional advantage.

For detonations, only crimped metal arresters are considered by the HSE *Guide*. It quotes the following equation for the maximum flame speed obtained by Cubbage (1959) for the stoppage of town gas–air mixture detonations by arresters with crimp height of 0.017 in.:

$$y = 1.3\,V^{\frac{1}{5}} - 4.4 \qquad [17.11.5]$$

The variables V and y are defined as in Equation 17.11.4.

The HSE *Guide* emphasizes the limited amount of work then available on the arrest of detonations.

The use of these equations requires data on flame speeds. Flame speed is a function not only of the flammable mixture but also of the system geometry. In particular, there exists a 'run-up' length over which there is a considerable acceleration of flame speed. The HSE *Guide* gives data on flame speed for several gas–air mixtures as a function of the run-up length in straight smooth pipes of up to 12 in. diameter.

For propane–air mixtures, the flame speeds given for run-up lengths of 1, 5, 10 and 35 ft are 16, 230, 330 and 330 ft/s, respectively, for ignition near the open end of the pipe, and 110, 380, 420 and 490 ft/s, respectively, for ignition near the closed end of the pipe. For other run

up distances the higher neighbouring flame speed value should be used.

These flame speeds for propane are typical of saturated hydrocarbons. There are, however, a number of substances, e.g. ethylene, which have higher flame speeds.

The HSE *Guide* also recommends that for certain substances, e.g. hydrogen, and for all substances in pipe lengths greater than 35 ft detonations giving pressures up to 500 psig should be assumed.

For propane–air mixtures, the detonation velocity is about 5800 ft/s. For town gas–air mixtures it is about 7000 ft/s. The HSE *Guide* gives the following equation for detonation velocity:

$$V = 300[(\gamma^2 - 1)Q]^{\frac{1}{2}} \qquad [17.11.6]$$

where Q is the heat of detonation (cal/g) of the gas mixture, V is the detonation velocity (ft/s), and γ is the ratio of specific heats of the gas mixture at the combustion temperature.

Equations 17.11.5 and 17.11.6 apply to gas mixtures at atmospheric temperature and pressure. At higher pressures flame speed is not greatly affected, but the volumetric heat release increases in proportion to absolute pressure. The effect of higher temperature is more complex. An increase in temperature raises the burning velocity but reduces the volumetric heat release.

If the flammable gas is mixed not with air but with oxygen or even oxygen-enriched air, there is a strong possibility of detonation. Such mixtures can give detonation velocities up to 12 000 ft/s and detonation pressures up to 1000 psig.

The basic design options are to keep the pipe length below 35 ft or to design for detonation. The former option includes the use of explosion relief vents to eliminate pipe runs of more than 35 ft.

If the pipe is not a straight smooth duct, but contains bends or obstacles, much higher flame speeds may be reached. A single right angle bend can cause a substantial increase in flame speed. In such cases it is necessary to use explosion relief much more liberally or to design for detonation.

17.11.10 Flame arresters: environment

As described above, flame arresters differ in their applications. Arresters also differ considerably in the environment in which they are required to function, particularly in-line arresters but also end-of-line arresters.

In discussing the environment of a flame arrester, H. Phillips and Pritchard (1986) consider (1) the upstream volume, (2) the arrester matrix and (3) the downstream volume. They define these regions in terms of the direction of flame propagation, which is not necessarily that of gas flow. This terminology is followed here, but in this section only.

The ignition source is by definition located in the upstream volume. The properties of the flame arriving at the arrester are determined by conditions in this space. These include the pressure, temperature and gas mixture composition. They also include the shape of the space, the run-up distance and, of great importance, features which affect the flow into the arrester. The authors cite cowls on end-of-line arresters and bends and obstacles in the pipework upstream of an in-line arrester.

Even if the arrester stops the flame from passing through, the hot gases leaving the arrester may reignite. Whether they do so depends on the conditions in the downstream volume. Reignition is governed by the balance between the heat generated by reaction of the hot gases leaving the arrester and the cooling due to mixing with cool gas or air. This mixing will depend on features tending to promote turbulence in the downstream space.

17.11.11 Flame arresters: testing

An account of British practice in the testing of flame arresters is given by H. Phillips and Pritchard (1986). They classify tests into (1) tests on end-of-line arresters, (2) deflagration tests on in-line arresters, (3) detonation tests on in-line arresters and (4) endurance burning tests.

One issue in the testing of arresters is definition of the conditions for which the arrester is to be tested. An arrester at a particular location may be required to deal with a number of different flame conditions.

Another issue is the selection of test gas mixtures which are representative of other mixtures of interest to the designer. One approach to this is to utilize the gas groups as defined in the standards on hazardous area classification, described in Chapter 16.

A third issue is the definition of the 'worst case' conditions.

The test conditions for end-of-line arresters typically involve low flame speeds and atmospheric pressure. Use is made of the hazardous area classification (HAC) gas groups, except for endurance burning.

The deflagration testing of in-line arresters is complicated by the fact that performance depends not only on flame speed but on pressure. A typical test sequence is to increase the run-up distance in lengths of straight pipe and determine the flame speed at which failure occurs. This procedure does not, however, take account of pressure, and experience indicates that it is not necessarily sufficient to use a safety factor based solely on the relation between run-up distance and flame speed at atmospheric pressure. In view of these problems, the authors recommend that an arrester be tested under conditions which approximate as closely as possible to those under which it is to be used.

The detonation testing of in-line arrester is usually based on a steady-state detonation, with CJ velocity. This does not allow for the possibility that the detonation may be overdriven. In a practical application it may be uncertain whether an overdriven detonation could occur.

The authors emphasize that an in-line arrester should be tested for both deflagration and detonation conditions. It should not be assumed that if the arrester is satisfactory for detonation, it will be so for deflagration also, since cases have occurred where this was not the case.

With regard to overdriven detonations, they state that it is uncertain whether flame arresters are effective against such detonations.

The arrester should be tested for its ability to stop a flame travelling from either direction.

A flame arrester must also pass an endurance burning test to ensure that it will not fail if a flame becomes stabilized on it. In this test the gas mixture is adjusted to obtain a maximum value for the flame temperature and

the endurance period of the arrester is then determined. Flashback of the flame should not occur during the test when the gas is turned off.

For this type of test the use of the HAC gas groups, based on the maximum experimental safe gap (MESG) and the minimum igniting current (MIC), is unsatisfactory. The authors discuss alternative approaches.

The testing of arresters is also discussed by W.B. Howard (1992a). He instances the case of a flame arrester which was found to be satisfactory for detonations of mixtures of air with propane but not with propylene, despite the fact that the comparable fundamental burning velocities of these two gases are comparable, being 46 and 52 cm/s, respectively.

The test procedures for in-line arresters utilize straight pipes. In practical applications the pipework is likely to contain features such as bends and valves.

Both sets of authors emphasize the unsatisfactory state of the art in the testing of flame arresters. There are a large number of arrester designs and a wide range of applications, with variations in system geometry, gas mixtures and ignition sources. There is a paucity of published scientific work on which general design methods might be based. The message is therefore that if there is doubt as to the suitability of an arrester in a particular application, tests should be conducted which simulate as closely as possible the set of worst case conditions in that application.

17.11.12 Flame arresters: codes and standards

Flame arresters are the subject of a number of codes and standards in different countries. These are reviewed by H. Phillips and Pritchard (1986) and W.B. Howard (1992a).

In the UK BS 7244: 1990 covers the testing of arresters, as described in the next subsection. In the USA the Underwriters Laboratories standard UL 525–1984 deals with construction and testing. Germany has legally backed standards on the same aspects, as described by Leineman (1970).

The International Maritime Organization (IMO) also has requirements for flame arresters (1984 MSC Circ. 373).

17.11.13 Flame arresters: BS 7244

The testing of flame arresters is covered by BS 7244: 1990 *Specification for Flame Arresters for General Use*. The standard requires that an arrester withstand a fixed number of flame and detonation tests without flame propagating through the arrester.

An account of the practicalities of testing against this standard is given by G.O. Thomas and Oakley (1993).

17.11.14 Flame arresters: design features

There are a number of design features which are crucial to the effectiveness of a flame arrester. These relate to (1) mechanical strength, (2) flame endurance, (3) instrumentation and (4) blockage avoidance.

For an in-line application, the arrester, its housing and the adjacent pipework should be able to withstand the shock from a detonation. This is a prime requirement in the selection of the type of arrester to be used.

The arrester element itself needs to have adequate mechanical strength. Use may be made of additional strengthening in the form of reinforcing grids across both faces of the arrester.

One expedient which is sometimes used to reduce the impact on the arrester is to set the arrester in a holder of enlarged cross-section. It has been found in practice that this does not always provide the degree of reduction of impact expected.

Another measure taken by some manufacturers is the provision of baffles to break up the detonation wave as it approaches the arrester, but there is little published on the performance of these devices.

An arrester, whether end-of-line or in-line, should be able to withstand a flame stabilized on it. An endurance burning test may be required to confirm this.

The instrumentation of arresters is discussed in the following section.

Both end-of-line and in-line arresters are subject to blockage. Both types are vulnerable to dust and corrosion products. An end-of-line arrester may also suffer blockage from sand, fibres and crystallized or polymerized vapours. There may also be more exotic forms of blockage such as birds nests.

Some protection may be afforded by the use of a screen on an end-of-line arrester or a filter for an in-line arrester.

In some installations the end-of-line arrester is heated to prevent blockage by condensed products. Where this is done it should be confirmed, by tests if necessary, that the arrester operates satisfactorily at the higher temperature.

With an end-of-line flame arrester there may be a risk to the plant from impingement of the flame.

A short vent pipe is sometimes used to prevent this. W.B. Howard (1992a) recommends that the arrester should be no more than five pipe diameters from the end of the pipe.

An in-line arrester generally presents an appreciable resistance to flow. Data on pressure drop through arresters have been correlated by Quinton (1962).

17.11.15 Flame arresters: instrumentation

An in-line flame arrester should be provided with instrumentation which will give an alarm to signal the presence of a flame and to take any appropriate protective action.

A common arrangement is two temperature sensors, one on each side of the arrester and close to it. The sensors should have rapid response and the trip level should be low enough to ensure effective protective action. If the sensors are sufficiently accurate, their response sequence can also indicate in which direction the flame has travelled.

The protective action might consist of the operation of fast-response isolation valves.

It is desirable to detect the presence of flame on an end-of-line arrester also, again using temperature sensors.

17.11.16 Flame arresters: inspection and maintenance

As a protective device, a flame arrester should be entered in the inspection schedule and inspected at suitable intervals.

It should have pressure tappings either side to allow the pressure drop across it to be measured. There should be adequate access to allow this to be done and to permit removal if necessary.

In general, a blocked arrester should be cleaned by blowing air or steam through it or by washing. It should not be cleaned, however, in any way which is liable to enlarge the apertures, such as rodding out.

17.11.17 Flame arresters: alternatives to arresters

It should not be assumed that a flame arrester is necessarily the right solution. Depending on the situation, it may be preferable to consider an alternative approach such as the use of automatic isolation or explosion suppression.

These alternatives are now briefly considered. They find application particularly in protection against dust explosions and a fuller account is given Section 17.47.

17.11.18 Automatic isolation

In some systems, the passage of an explosion from one section to another may be prevented by automatic high speed isolation. An account of this method is given in FPA FS 6012: 1989 *Flammable Liquids and Gases: Explosion Control.*

A typical installation is illustrated in Figure 17.17. Very rapid detection and valve closure are necessary.

The design of such a system requires information on the rate of pressure rise caused by the expected explosion. This information is also required for the design of automatic explosion suppression systems and is discussed below in relation to the latter. From the data on the rate of pressure rise a suitable high speed detector can be chosen. The shut-off valve must also operate very quickly. One method of achieving rapid closure is the use of explosives.

Isolation protects only the section isolated and not the section in which the explosion occurs. The application of automatic high speed isolation appears to be fairly limited.

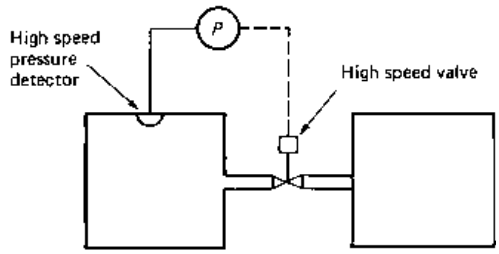

Figure 17.17 *System for automatic isolation installed in a pipe*

17.11.19 Automatic explosion suppression

A developing explosion may be detected and suppressed using an automatic high speed suppression system.

Accounts of automatic explosion suppression are given in FPA FS 6012: 1989 and FS 6015: 1974 *Explosible Dusts, Flammable Liquids and Gases: Explosion Suppression* and by Grabowski (1965) and K.N. Palmer (1973a).

A typical explosion suppression system in a pipe is illustrated in Figure 17.18.

An explosion suppression system for a vessel, and the principles of operation of such system, are shown in Figure 17.19. Again very rapid detection and suppression are required.

The basic data for the design of an explosion suppression system are given by the explosion pressure curve for the gas. A typical curve is shown in Figure 17.20 as curve 1.

This information is used to estimate the required response time of the detector and of the suppressant in order to limit the explosion pressure to a specified value. The pressure response typically obtained with explosion suppression is shown in curve 2 of Figure 17.20.

Broadly, the rate of rise of pressure follows the cube law given in Equation 17.7.48, as described in Section 17.7, but factors such as vessel geometry and turbulence effects make prediction difficult.

The main suppressants used are halons such as bromochlorodifluoromethane and chlorobromomethane, and water. The quantity of liquid agent commonly specified is $2.14\,l/m^3$ of protected space. The suppressant is discharged by an electrically fired detonator within 1 ms of the closure of the detonator contacts.

The size and shape of vessel to which explosion suppression can be effectively applied is not unlimited. FS 6015: 1974 stated that explosion suppression is applicable to vessels with a volume of up to $115\,m^3$ and for flammable gas mixtures for which the maximum explosion pressure is generated in not less than 40 ms.

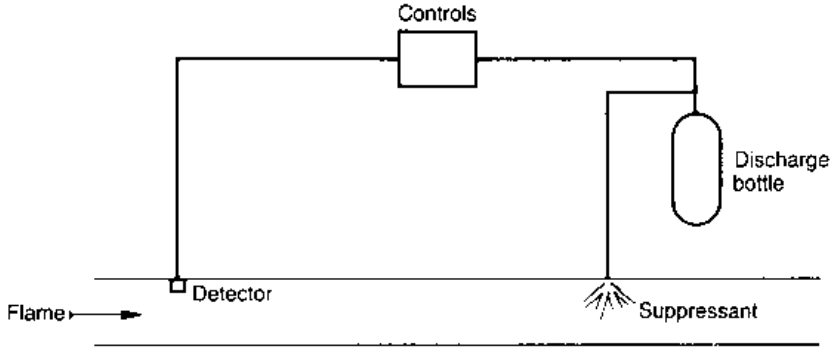

Figure 17.18 *System for automatic explosion suppression installed in a pipe*

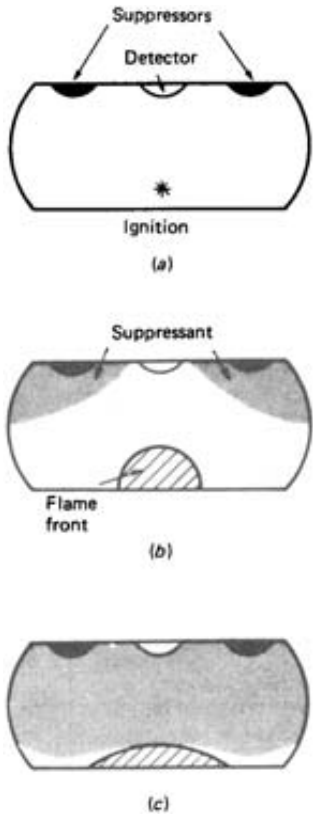

Figure 17.19 *System for automatic suppression of an explosion in a vessel (after Fire Protection Association, 1974 FS 6015): (a) initial ignition; (b) suppressors activated; (c) suppression nearly complete*

Developments in technology have tended to expand these limits, as described in relation to dusts in Section 17.47.

With an automatic explosion suppression system operating, the maximum pressure of the suppressed explosion is typically reached in about 10 ms.

A potential disadvantage of automatic explosion suppression is the risk of spurious trips. This has not proved sufficiently serious, however, to discourage its use.

Automatic explosion suppression systems are widely used.

17.11.20 Explosion relief and venting

A quite different approach is to relieve the explosion by venting. Explosion venting is applied to (1) vessels, (2) pipes and ducts, (3) buildings, (4) large enclosures, (5) reactors and (6) storage vessels.

If this option is adopted, it is necessary to consider not only the venting itself, but also the disposal of the material vented, which may not be a trivial problem.

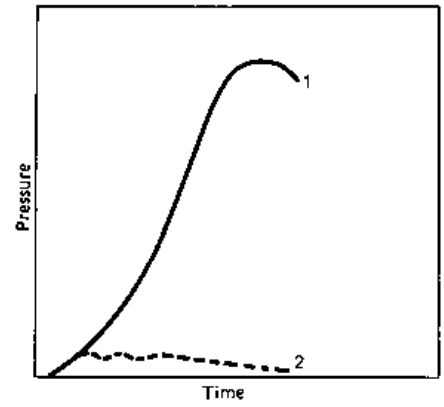

Figure 17.20 *Typical explosion pressure curves for an automatic suppression system: curve 1, explosion pressure in absence of suppression; curve 2, explosion pressure with suppression operating*

Explosion relief of vessels is treated in Section 17.12, of pipes and ducts in Section 17.13, of buildings in Section 17.14, of large enclosures in Section 17.15 and of reactors in Sections 17.16–17.23.

17.12 Explosion Venting of Vessels

One of the options for the protection of a vessel against a gas explosion is the use of explosion venting, also referred to as explosion relief.

Accounts of explosion venting are given in *Explosions* (Bartknecht, 1981a), *Development and Control of Dust Explosions* (Nagy and Verakis, 1983), *Gas Explosions in Buildings and Heating Plants* (R.J. Harris, 1983) and *Venting Gas and Dust Explosions – A Review* (Lunn, 1984b, 1992). All of these except the book by Harris also deal with dust explosions.

Explosion venting is also dealt with in NFPA 68: 1994 *Deflagration Venting.*

The notation used in explosion venting is particularly liable to cause confusion. The term 'maximum explosion pressure' refers generally to a closed, or unvented, explosion, but occasionally it refers to a vented explosion. Pressure is defined sometimes as an absolute pressure, sometimes as a gauge pressure and sometimes as a pressure in excess of the initial pressure. Many of the principal equations were developed originally in British units. Where SI units are used, pressure is generally expressed not in pascals but in kilopascals or bar.

In the account given here, the pressure in a vented system is referred to as the reduced pressure, P_{red}. Explosion venting of vessels is a topic in which there are a large number of empirical equations in particular sets of units. Some equations are quoted here in their original form in British units, but generally the use of SI units is preferred. However, with the latter, unless otherwise stated, where units are given, the common practice of giving pressure in kilopascals has been followed. In some subsections equations are given without units, and in

these cases any consistent set of units is applicable. Further information on the units used is given in the Notation.

The definition of reduced pressure P_{red} as absolute or gauge is not always clearly stated in the original papers and sometimes has to be inferred.

17.12.1 Factors influencing explosion venting

The various factors which influence the maximum pressure and the rate of rise of pressure in an explosion in a closed vessel were described in Section 17.7. They are relevant to vented explosions also.

One factor which assumes particular significance for a vented explosion is the location of the ignition source. Different models have been developed for vented explosions with different locations of the ignition source, as described below.

17.12.2 Experimental studies of venting

There have been a number of experimental studies of explosion venting. Some of the principal studies are listed in Table 17.14.

Early work on explosion relief was done by Cousins and Cotton (1951a,b), who studied a range of containers with L/D ratios varying from 1.41 to 22.1. The relief was a bursting disc. The gases used were propane and hydrogen.

Another early study was carried out at the Midlands Research Station (MRS) of the Gas Council by Cubbage and Simmonds (Cubbage and Simmons, 1955a,b; Simmonds and Cubbage, 1960). Their work was concerned with the explosion venting of industrial drying ovens. The experiments were done on ovens which were approximately cubical and with a variety of vent conditions. The principal gas used was town gas. The pressure profile resulting from an explosion with explosion relief was of the form shown in Figure 17.21. The initial pressure peak at A was followed by a second, higher peak at B.

Other experimental studies which have yielded data sets against which correlations can be tested include those of Burgoyne and Wilson (1960), G.F.P. Harris and Briscoe (1967), Yao and co-workers (Yao *et al.*, 1969; Yao, 1974) and Zalosh (1980b).

Experimental studies on larger containments which are often referred to in relation to explosion venting of vessels include those of the Committee for Explosion Research (1958) in Sweden, Dragosavic (1973), Solberg, Pappas and Skramstad (1980, 1981) and Buckland (1980).

17.12.3 Phases of vented explosion

A vented explosion passes through three phases: the initial confined explosion phase, the vent removal phase and the venting phase.

The pressure–time profiles obtained in venting experiments may exhibit as many as three peaks, although in many cases one or more of these peaks is absent or runs into another peak. Explanations of this multiple-peak behaviour have been given by Anthony (1977/78), R.J. Harris (1983) and Lunn (1984b).

Table 17.14 *Explosion venting of vessels: some experimental studies*

	Vessel or enclosure			
Investigator(s)	*Type and dimensions* (m)	*Volume* (m^3)	*Relief*	*Gas mixture*
Cousins and Cotton (1951a)	(1) Drum, 0.59 diam. × 0.84; L/D 1.41	0.215		Propane, hydrogen
	(2) Tank, 0.36 diam. × 0.823 length; L/D 2.3	0.085		
	(3) Vessel, 0.305 diam. × 0.469 height	0.032		
	(4) Pipe, 0.28 diam. × 6.22 length	0.40		
Cubbage and Simmonds (1955a–c)	Cubical drying ovens	≤14	Vent	Town gas, methane
Burgoyne and Wilson (1960)	Cylindrical chamber, 1.27 diam.	1.7, 5.7	Bursting disc	Pentane
G.F.P. Harris and Briscoe (1967)	Vessel, 1.37 diam. × 1.45 length	1.7		
Yao *et al.* (1969); Yao (1974)	(1) Cubical chamber, 0.91 × 0.91 × 0.91	0.765	Open vent	Propane, hydrogen
	(2) Cylindrical chamber, 0.91 diam. × 0.91 length	0.786	Bursting diaphragm	
	(3) Cylindrical chamber, 0.91 diam. × 2.74 length	2.36		
Zalosh (1980b)	Rectangular enclosures:		Vent	Methane, propane, ethylene
	(1) 0.92 × 0.61 × 0.31	0.17		
	(2) 0.56 × 0.56 × 0.56	0.18		
	(3) 0.71 × 0.71 × 0.37	0.19		
	(4) 1.47 × 0.91 × 0.43	0.58		
	(5) 1.80 × 2.00 × 3.10	11.2		
	(6) 5.40 × 2.00 × 3.10	33.5		

The first peak occurs when the vent opens. The magnitude of this peak is a function of the vent opening pressure P_v and the vent inertia w.

The second peak is associated with an increase in the rate of combustion as the burned gas core grows. The magnitude of this peak is a function of two factors. One is the features which may give an enhanced combustion rate. These include shear turbulence and stretching of the flame towards the vent. The other factor is the flow resistance, which depends on the vent size and on any vent ducting.

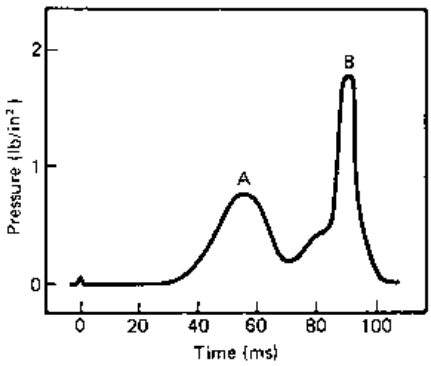

Figure 17.21 *Explosion venting of vessels: typical explosion pressure curve obtained in explosion venting of an enclosure in work of Cubbage and Simmonds (after Simmonds and Cubbage, 1960) (Courtesy of the Institution of Chemical Engineers)*

The third peak is associated with the venting of burned gas. When the burned gas starts to vent, the volumetric flow increases markedly, since the burned gas density is much less than that of the unburned gas.

The first peak may be weak or absent if the vent is an open one. It tends to be large if the vent opening pressure or vent inertia are high. But if the vent area is small so that there is little vent outflow before the second peak arrives, the first peak merges into the second one. This may also occur if the vent opening pressure is sufficiently high.

The second peak may be weak if the rate of combustion is slow or the vent area large. Conversely it is large if the rate of combustion is high and the vent area is small. In the former case the second peak may merge into the first one.

In the later stages of venting the explosion may exhibit various types of oscillatory behaviour as evidenced by the pressure trace.

Some typical pressure profiles are illustrated in Figure 17.22. Other examples of the multiple peaks obtained in explosion venting are given in Section 17.15.

Another feature of the venting process is the effect of the vent pressure on the combustion process. For a vessel with a relatively low vent area, if the vent pressure is set at a low value, the explosion pressure tends to exceed the vent pressure. The phenomenon has been studied by G.F.P. Harris and Briscoe (1967), who attribute it to a large increase in the flame area when the vent is opened. This is illustrated in Figure 17.23.

The development of the flame kernel during venting of an explosion in a vessel is shown in Plate 15.

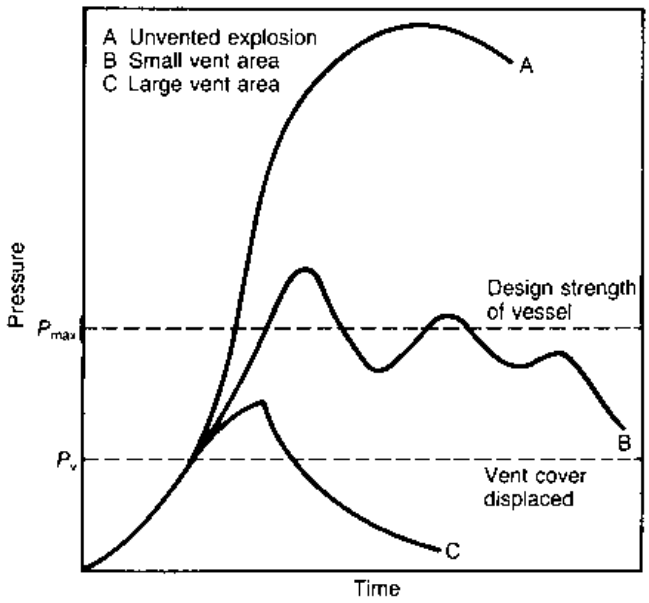

Figure 17.22 *Explosion venting of vessels: generalized explosion pressure curves for closed and vented vessels (Field, 1982; reproduced by permission of Elsevier Science Publishers)*

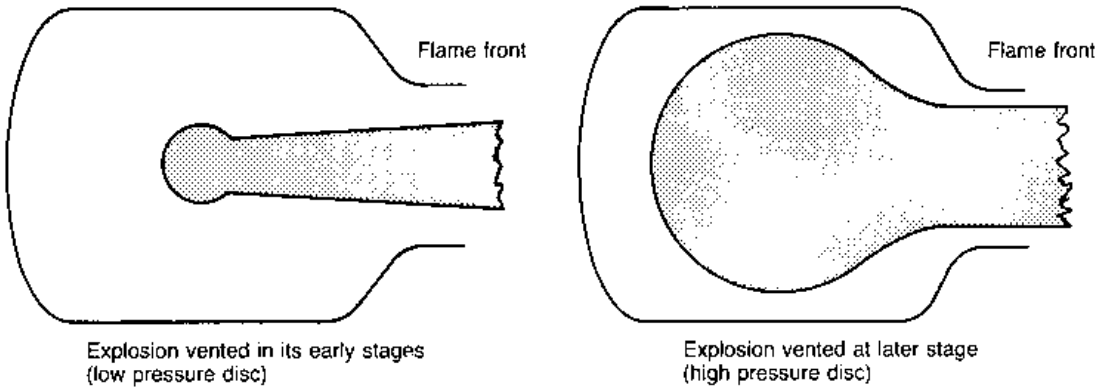

Figure 17.23 *Explosion venting of vessels: distortion of flame front on opening of vent (G.F.P. Harris and Briscoe, 1967) (Courtesy of the Combustion Institute)*

17.12.4 Oscillatory behaviour

Pressure–time profiles of a vented explosion often show marked oscillatory behaviour in the later stages. The significance of this is that combustion oscillations can greatly increase the combustion rate, particularly in the later stages, and can result in higher pressures. The effect becomes relatively more important as the scale increases, but it may not be negligible even for vessels.

Oscillation in explosion venting was described by Zalosh (1980b), who obtained high, delayed, oscillatory second peaks in the pressure–time profile using propane.

Oscillatory behaviour in explosion venting of a spherical vessel with a vent tube attached has been investigated by Kordylewski and Wach (1988).

One type of oscillatory behaviour is that due to acoustic oscillation. For an acoustic oscillation Kordylewski and Wach used the relation

$$f_a = \frac{c\lambda_1}{2\pi r_s} \qquad [17.12.1]$$

where c is the speed of sound in the medium, f_a is the frequency of the oscillation, r_s is the radius of the spherical vessel and λ_1 is a constant. The value of λ_1 is 4.4934.

Formulae for this and other geometries are given in *Formulas for Natural Frequency and Mode Shape* (Blevins, 1979).

Another type of oscillatory behaviour is that due to Helmholtz oscillation. For Helmholtz oscillation Kordylewski and Wach used the relation

$$f_H = \frac{c}{2\pi}\left(\frac{A_v}{L + \alpha V}\right)^{\frac{1}{2}} \qquad [17.12.2]$$

with

$$\alpha = 0.255D \qquad [17.12.3]$$

where A_v is the vent area, D is the duct diameter, f_H is the frequency of Helmholtz oscillation, L is the length of the duct, V is the volume of the vessel and α a correction factor.

The occurrence and strength of combustion oscillations depend on the concentration of the gas mixture. Thus in the work of Zalosh (1980b) just described, oscillations were observed for propane concentrations only in the range 5.0–5.5%.

The oscillations tend to be more marked just on the fuel rich side of the stoichiometric ratio. C.J.M. van Wingerden (1989c) found, using 9.5 and 10% methane–air mixtures, that whilst the former was the stoichiometric concentration it was the latter which was more sensitive to oscillatory combustion.

17.12.5 Empirical and semi-empirical methods

As already indicated, the venting of an explosion is a complex process. It is therefore difficult to model theoretically. This has led to the development of a number of empirical and semi-empirical methods and of scaling laws.

17.12.6 Vent ratio and vent coefficient

Work on explosion venting makes frequent use of two quantities, the vent ratio and the vent coefficient. The vent ratio f is defined as the ratio of the vent area A_v to the volume vented V:

$$f = A_v/V \qquad [17.12.4]$$

The vent coefficient K is defined as

$$K = A_c/A_v \qquad [17.12.5]$$

with

$$A_c = L_1 L_2 \qquad [17.12.6]$$

where A_c is the area of the smallest cross-section of the enclosure (m^2), A_v is the vent area (m^2), K is the vent coefficient, and L_1 and L_2, for a rectangular enclosure, are the dimensions of the two smallest sides (m).

The vent coefficient is therefore dimensionless, but the vent ratio is not.

These two quantities are discussed further below, particularly in relation to scaling methods.

17.12.7 Rasbash method

An early equation for the reduced pressure P_{red} in a vented explosion, or vented explosion pressure, was that of Rasbash (1969c), who gave the following equation for

the maximum pressure in a vented explosion in a building:

$$P_{red} = 1.5P_v + 0.5K \quad [17.12.7]$$

with

$$K = A_c/A_v \quad [17.12.8]$$

where A_c is the area of the smallest cross-section of the enclosure (ft^2), A_v is the total area of combustion vents (ft^2), K is the venting ratio, P_{red} is the reduced pressure, or maximum pressure reached during the venting of combustion (gauge) ($lb_f/in.^2$), and P_v is the pressure within the building space at which the vent opens (gauge) ($lb_f/in.^2$). In SI units these equations become

$$P_{red} = 1.5P_v + 3.5K \quad [17.12.9]$$

with

$$K = A_c/A_v \quad [17.12.10]$$

where A_c is the smallest cross-sectional area of the endosure (m^2), A_v is the total area of combustion vents (m^2), K is the venting ratio, P_{red} is the reduced pressure (gauge) (kPa) and P_v is the pressure within the building space at which the vent opens (gauge) (kPa).

Rasbash stated that Equation 17.12.9 was based on a collation of information on experimental work on venting using particularly propane and referred to work on explosion relief of ducts (Rasbash and Rogowski, 1960b).

There are a number of restrictions on the use of Equation 17.12.9. They may be summarized as

$$L/D < 3;\ 1 \le K \le 5;\ w \le 24;\ P_v \le 7$$

where w is the inertia of the vent (kg/m^2). In addition, the pressure should be virtually exhausted after the vent has moved a few millimetres.

Equation 17.12.9 applies to propane. For natural gas and for town gas which contains 60% H_2, the pressures reached are, respectively, about 0.8 and 2.5 times that given by Equation 17.12.9 (Mainstone, 1971).

If the flammable mixture is turbulent when ignited or becomes turbulent during the combustion, pressures considerably higher than those given in Equation 17.12.9 may be generated.

In subsequent work, Rasbash, Drysdale and Kemp (1976) modified Equation 17.12.9 to include a term for the vent inertia

$$P_{red} = AP_v + P_I + BK \quad [17.12.11]$$

with

$$P_I = \frac{0.203Kw + 1.17}{V^{\frac{1}{3}}} \quad [17.12.12]$$

$$w = W_v/A_v \quad [17.12.13]$$

where P_I is the back pressure due to the inertia of the vent (gauge) (kPa), w is the inertia of the vent (kg/m^2) and W_v is the mass of the vent cover (kg). The values of the constants given are 1–1.5 kPa for A and 2.5 kPa for B; the value commonly used for A is 1.5.

The authors then generalize Equation 17.12.11 to make it applicable to other flammable gases:

$$P_{red} = 1.5P_v + S_u(P_I + 2.5K)/0.45 \quad [17.12.14]$$

where S_u is the maximum fundamental burning velocity (m/s). The constant 0.45 represents the maximum fundamental burning velocity of propane.

Finally, Rasbash, Drysdale and Kemp introduce a turbulence factor f so that Equation 17.12.14 becomes

$$P_{red} = 1.5P_v + fS_u(P_I + 2.5K)/0.45 \quad [17.12.15]$$

They suggest for f a value of 1.5 for a single room, but modify this considerably for certain conditions. For a situation where the explosion propagates from one room to another they propose for f a value of 5, and for a high pressure leak of liquid petroleum gas (LPG) values of 8 or even 10.

For comparison with equations derived by other workers it is helpful to combine Equations 17.12.11 and 17.12.12, to give

$$P_{red} = 1.5P_v + \frac{0.20KwS_u}{0.45V^{\frac{1}{3}}} + \frac{1.17S_u}{0.45V^{\frac{1}{3}}} + \frac{2.5S_uK}{0.45} \quad [17.12.16]$$

The relative importance of the terms in Equation 17.12.16 may vary. If P_v is high, P_{red} approximates to it, whilst if P_v is low, P_{red} may be appreciably higher than P_v. If K is low (high A_v), P_{red} approximates to P_v, whilst if K is high, P_{red} may again be higher than P_v.

Equation 17.12.11 has been widely used for the explosion relief of buildings. It is considered further in Section 17.14.

17.12.8 Cubbage and Simmons method

The pressure profile obtained by Cubbage and Simmonds in their work on drying ovens was described above. The relation obtained by these authors for the first pressure peak (peak A in Figure 17.21) is

$$P_1 = \frac{0.437KwS_u}{V^{\frac{1}{3}}} + \frac{2.817S_u}{V^{\frac{1}{3}}} \quad [17.12.17]$$

and that for the second peak (peak B in Figure 17.21) is

$$P_2 = 5.8S_uK \quad [17.12.18]$$

where K is the vent coefficient, P_1 and P_2 are respectively the first and second pressure peaks (gauge) (kPa), S_u is the maximum fundamental burning velocity (m/s), V is the volume of the vessel (m^3) and w is the inertia of the vent (kg/m^2).

In contrast to Rasbash's method, Cubbage and Simmonds's method is based on separate equations for the two pressure peaks. The first of their equations depends only on the inertia w of the vent panel, the second only on the vent coefficient K, whilst the vent opening pressure P_v does not appear.

17.12.9 Runes method

In contrast to the two empirical correlations just described, the equation given by Runes (1972) for the vent area of a large container or building has some theoretical basis. It is based on equating the volume production rate and the volumetric vent outflow. The volume production rate is

$$Q_m = A_m V_f(E - 1) \quad [17.12.19]$$

with

$$A_m = \pi L_1 L_2 \quad [17.12.20]$$

where A_m is the maximum area of the flame front (ft^2), E is the expansion ratio, L_1 and L_2 are the two smallest dimensions of the enclosure (ft), Q_m is the rate of volume production (ft^3/s) and V_f is the flame speed (ft/s).

The volumetric vent outflow is

$$Q_v = YC_dA_v(2g \times 144\ \Delta P/\rho)^{\frac{1}{2}} \quad [17.12.21]$$

where C_d is the coefficient of discharge, g is the acceleration due to gravity (ft/s^2), ΔP is the vented explosion pressure (gauge) ($lb_f/in.^2$), equivalent to P_{red}, Q_v is the volumetric vent outflow (ft^3/s), Y is a constant which takes account of the expansion of the gas as it discharges and ρ is the density of the gas (lb/ft^3). The value of C_d is 0.6, and Y is usually unity.

Runes takes $Y = 1$, $C_d = 0.6$, $g = 32.2$ and $\rho = 0.085$, and obtains

$$Q_v = 200A_v\ \Delta P^{\frac{1}{2}} \quad [17.12.22]$$

(Equation 17.12.22 is obtained from Equation 17.12.21 by substituting the numerical values given by Runes. He actually gives not Equation 17.12.21 but one in which the right hand side is $YC_dA_v2g(144\,\Delta P)^{\frac{1}{2}}/\rho$, but this is evidently a typographical error. This error has caused some confusion in the expressions quoted in the literature for the Runes constant C, described below.)

Then from Equations 17.12.19, 17.12.20 and 17.12.22

$$A_v = \frac{\pi L_1 L_2 V_f (E-1)}{200\ \Delta P^{\frac{1}{2}}} \quad [17.12.23]$$

$$= \frac{CL_1L_2}{\Delta P^{\frac{1}{2}}} \quad [17.12.24]$$

with

$$C = \frac{\pi V_f (E-1)}{200} \quad [17.12.25]$$

where C is a constant.

The value of the constant C is discussed in more detail in Section 17.14 on explosion venting of buildings. Runes himself did not assign a value to the constant, though from Equation 17.12.25 $C = 0.108V_f$. As described in Section 17.14, W.B. Howard (1972) assigned a value to C of 1.2 by inserting the value for propane of $V_f = 11$ ft/s. However, in the same paper Howard also made his own calibration of the constant based on an incident involving ethanol for which he took $V_f = 24$ ft/s and thus obtained a value of $C = 2.6$ ($1.2 \times 24/11$).

The constant C is best regarded as an empirical one which allows for the actual flame speed under the conditions of turbulence in the enclosure. NFPA 68: 1978 gives for C in British units for use in Equation 17.12.24 a value of 2.6 for gases such as propane and other gases with a similar burning velocity. A higher value is recommended for gases with a higher burning velocity. The suggested value for ethylene is 4 and that for hydrogen 6.4.

In SI units Equation 17.12.24 is

$$A_v = C\frac{L_1L_2}{\Delta P^{\frac{1}{2}}} \quad [17.12.26]$$

where A_v is the necessary building vent area (m^2), L_1 is the smallest dimension of the rectangular building enclosure to be vented (m), L_2 is the second smallest dimension of that building (m), P the maximum internal building pressure (gauge) (kPa) and C is a constant.

NFPA 68: 1978 gives for C in metric units for use in Equation 17.12.26 a value of 6.8 for gases such as propane and others gases with a similar burning velocity, whilst the suggested value for ethylene is 10.5 and that for hydrogen is 17.

Equation 17.12.26 has been widely used for the explosion relief of buildings. It is considered further in Section 17.14. NFPA 68: 1994 gives a relationship similar to Equation 17.12.26; this is described in Section 17.14.

17.12.10 Decker method

The method described by Decker (1971) is based on somewhat similar considerations to that of Runes. The approach is again to equate the volume production rate and the volumetric vent outflow;

$$Q_v = \frac{dP}{dt}\frac{V}{P_v} \quad [17.12.27]$$

$$= V/t \quad [17.12.28]$$

where P is the pressure ($lb_f/in.^2$), P_v is the vent pressure ($lbf/in.^2$), Q_v is the volumetric vent outflow (ft^3/s), t is time (s) and V is the volume of the vessel (ft^3).

For the vent area he then obtains

$$A_v = k\frac{dP}{dt}V\left(\frac{\bar{M}}{T}\right)^{\frac{1}{2}}\frac{1}{P_v} \quad [17.12.29]$$

where A_v is the vent area (ft^2), $\bar{M}$ is the mean molecular weight of the gas, T is the absolute temperature of the burnt gases (°R) and k is a constant. The value of the constant k is 1/132. The temperature T of the burnt gases is of the order of 3600°R.

The treatment by Lowenstein (1958) is rather similar.

17.12.11 Dragosavic method

Dragosavic (1973) has given equations for the first and second peak pressures in explosions in rooms in dwellings. For the first peak pressure

$$P_1 = P_v + C \quad [17.12.30]$$

and for the second peak pressure

$$P_2 = AP_v + B/\psi^2 + C \quad [17.12.31]$$

with

$$\psi = A_v/V \quad [17.12.32]$$

where P_1 and P_2 are respectively the first and second peak pressures (gauge) (kPa), P_v is the vent opening pressure (kPa), ψ is a vent ratio (m^{-1}), and A, B and C are constants. The values of A, B and C for natural gas–air mixtures are 0.5, 0.04 and 3.0 kPa, respectively. Equation 17.12.30 applies to enclosures with open and closed vents. Equation 17.12.31 represents an envelope of the experimental values and therefore overestimates the second peak pressure.

17.12.12 Cubbage and Marshall method

Cubbage and Marshall (1973) have obtained the relation

$$P_{red} = P_v + 2.44(KwS_u^2/V^{\frac{1}{3}}) \quad [17.12.33]$$

where K is the venting coefficient, P_{red} is the reduced pressure (gauge) (kPa), P_v is the vent opening pressure

(gauge) (kPa), S_u is the maximum fundamental burning velocity (m/s), V is the volume of the vessel (m^3) and w is the inertia of the vent (kg/m^2).

17.12.13 Other methods

The following further equations for explosion venting are quoted by Lunn. Rasbash has given the two equations

$$P_{red} = P_v + 7.76 S_u K \quad [17.12.34]$$

$$P_{red} = (P_v + 7.76K) S_u K \quad [17.12.35]$$

where K is the venting coefficient, P_{red} is the reduced pressure (gauge) (kPa), P_v is the vent opening pressure (gauge) (kPa) and S_u is the fundamental burning velocity (m/s).

Burgoyne and Wilson (1960) have given the following equation for their work on pentane–air systems:

$$P_{red} = 68 \log_{10}(K) - 28.6 \quad [17.12.36]$$

where K is the venting coefficient and P_{red} is the reduced pressure (gauge) ($lb_f/in.^2$).

17.12.14 Scaling methods

Empirical equations have the limitation that they cannot be used with confidence outside the range of experimental data on which they are based. An alternative empirical approach is the use of scaling laws validated over a wide range of experimental conditions.

There are two principal methods based on scaling laws which are used for gas explosion venting: the vent ratio method and the vent coefficient method. Traditionally, in Britain the vent coefficient method has been used for venting of gas explosions and the vent ratio method for venting of dust explosions, but there is no logical basis for this.

17.12.15 Vent ratio method

The vent ratio f is defined as

$$f = A_v / V \quad [17.12.37]$$

where A_v is the vent area, f is the vent ratio and V is the volume of the enclosure.

The simple application of the vent ratio method is the use of a constant vent ratio.

It is found in practice that in scaling up from small scale tests the use of a constant vent ratio tends to overestimate the vent area required. The following alternative treatment given by Lunn addresses this problem. The relationship between the rate of pressure rise and the volume of the vessel is given by the cube root law

$$\frac{dP}{dt} V^{\frac{1}{3}} = \text{constant} \quad [17.12.38]$$

Following an approach similar to that of the Decker method, as given in Equation 17.12.29, but using P_{red} rather than P_v, the volumetric venting flow Q_v, and hence the vent area required, is

$$A_v \propto \frac{dP}{dt} \frac{V}{P_{red}} \quad [17.12.39]$$

Hence for the vent ratio

$$f V^{\frac{1}{3}} = \text{constant} \quad [17.12.40]$$

This approach implies that the cube root law is applicable to vented vessels also. It is the basis of the Bartknecht nomograph method described below.

A common method of characterizing the vent area required is to plot the reduced explosion pressure as a function of vent ratio. Numerous such plots are given by Lunn.

17.12.16 Vent coefficient method

The vent coefficient K is defined as

$$K = A_c / A_v \quad [17.12.41]$$

with

$$A_c = L_1 L_2 \quad [17.12.42]$$

where A_c is the area of the smallest cross-section of the enclosure, K is the vent coefficient and L_1 and L_2 are the two smallest dimensions of the enclosure.

For a cubical enclosure of volume V

$$A_c = V^{\frac{2}{3}} \quad [17.12.43a]$$

$$L_1 L_2 = V^{\frac{2}{3}} \quad [17.12.43b]$$

The following treatment by Lunn gives the relation between the vent coefficient and the reduced pressure. Again following Decker and using Equation 17.12.29 with P_{red} together with Equations 17.12.38, 17.12.41 and 17.12.43

$$P_{red} \propto K \quad [17.12.44]$$

The characteristics of the vent ratio and vent coefficient methods have been explored by N. Gibson and Harris (1976), as shown in Figure 17.24. Their experimental results for pentane, and also those for class St 2 dusts, are well fitted using the vent coefficient with $K = 3$. Also shown are curves for various vent ratios. The two methods exhibit an increasing divergence in the predicted vent areas as the vessel volume increases.

A critique of vent coefficient scaling has been given by Zalosh (1980b). He carried out experiments with a range of containment volumes from 0.17 to 33.5 m^3, and found that such scaling is valid for volumes up to 12 m^3 but that for larger volumes the relationship breaks down due apparently to effects related to flame speed.

17.12.17 K_G method

The K_G method developed by Bartknecht is based on the cube root law given in Equation 17.12.38. The cube root law in terms of the maximum rate of pressure rise is

$$\left(\frac{dP}{dt}\right)_{max} V^{\frac{1}{3}} = K_G \quad [17.12.45]$$

and in terms of the rate of pressure rise with venting

$$\left(\frac{dP}{dt}\right)_{P_{red}} V^{\frac{1}{3}} = K_G \quad [17.12.46]$$

Thus for the same reduced pressure the vent ratio f also follows the cube root law

$$f V^{\frac{1}{3}} = \text{constant} \quad [17.12.47]$$

As described by Bartknecht (1981a), Donat and Bartknecht have carried out extensive experimental work on vented explosions using the Ciba-Geigy 20 litre sphere. They apply the cube root law of Equation

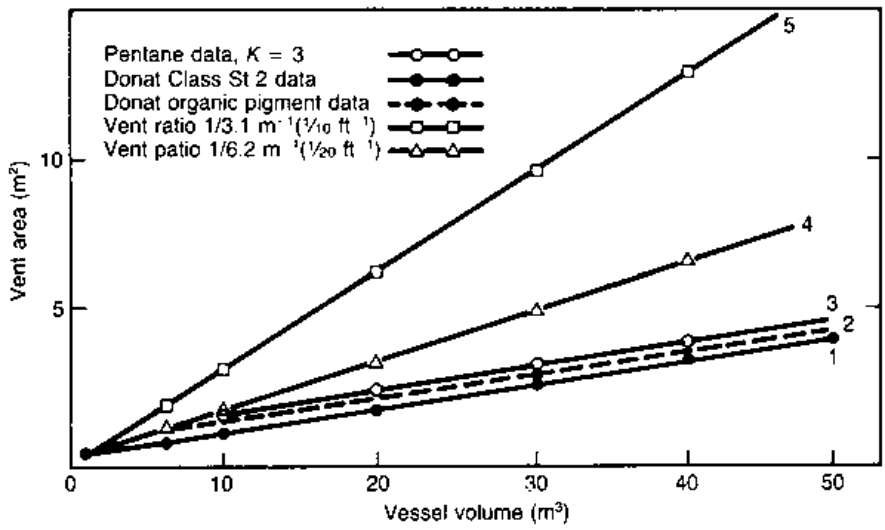

Figure 17.24 *Explosion venting of vessels: some vent ratio and vent coefficient predictions (N. Gibson and Harris, 1976): (1) Donat's results for St 2 dust; (2) Donat's results for organic pigment; (3) results for pentane with vent coefficient K = 3; (4) vent ratio 1/6.2 m^2/m^3; and (5) vent ratio 1/3.1 m^2/m^3. Maximum pressure rise 48 kPa and vent rupture pressure 7–14 kPa. (Courtesy of the American Institute of Chemical Engineers)*

17.12.45 and determine the value A_v for values of the gas factor K_G, the vent opening pressure P_{stat} and the reduced explosion pressure P_{red}.

The results of their work are given in the form of a series of nomographs for the determination of the vent area A_v for particular values of the vessel volume V, the initial pressure P_o and the vent explosion pressure P_{red}. Each nomograph is for a particular value of K_G, degree of initial turbulence and strength of ignition source. For gases the values given for K_G are as follows:

	K_G (bar m/s)
Methane	55
Propane	75
Coke gas	140
Hydrogen	550

For solvents the value used is that for propane.

The nomographs give the vent area A_v as

$$A_v = f(V, K_G, P_{stat}, P_{red}) \quad [17.12.48]$$

where P_{red} is the reduced pressure, and P_{stat} the vent opening pressure and V is the volume of the vessel.

The derivation of these nomographs has been described by Lunn, Brookes and Nicol (1988) and in NFPA 68: 1994, and is discussed further in Section 17.48.

There is a separate nomograph for each of the four gases mentioned. The vent opening pressure P_{stat} is given as a parameter. The three values of P_{stat} are 0.1, 0.2 and 0.5 barg. The range of values of P_{red} is 0.2–2.0 barg.

The nomographs are valid within a limited range of conditions. They are for a quiescent mixture and a weak ignition source (10 J). Their use is not recommended for $V > 1000\,m^3$, $P_{stat} < 0.1$ barg and $P_{red} < 0.2$ or >2.0 barg.

Experiments have shown that above a reduced pressure P_{red} of 2.0 barg, a well defined correlation of P_{red} cannot be obtained, which is the reason for the upper limit in the nomographs.

The K_G nomograph method was adopted in NFPA 68: 1988, and the nomographs in Figure 17.25 are those given in the current version NFPA 68: 1994.

The use of the nomographs is illustrated in Figure 17.26. For a vessel of volume V, enter on the right hand graph, move up to the desired value of the reduced pressure P_{red}, move left on the left hand graph to the desired value of the vent opening pressure P_{stat} and then move down to the required vent area A_v.

The vent area given by the nomographs is illustrated in Figure 17.27 for a $1\,m^3$ vessel with a vent opening pressure $P_{stat} = 0.1$ barg.

The nomographs may be used for other gases by interpolation of the K_G values. They may be used for stronger ignition sources if the K_G value for the gas with that ignition source is known.

In Bartknecht's method, if the mixture is not quiescent, the effect of turbulence must be taken into account. The information available on this is limited. But for large vent area A_v and low reduced pressure P_{red} (≤ 2 bara) turbulence has little effect and the nomographs may be used as they stand. For small A_v and high P_{red} (>2 bara) A_v should be increased by a correction term ΔA_v, where

$$\Delta A_v = 0.08 V^{\frac{2}{3}} \quad [17.12.49]$$

Bartknecht states that this treatment is applicable only to methane, propane and solvent vapours and for $P_{stat} \leq 0.1$ barg.

Table 17.15 *Explosion venting of vessels: values of parameters for an equation equivalent to the Bartknecht nomographs (after Simpson, 1986) (Courtesy of American Institute of Chemical Engineers)*

	Parameter			
Gas	a	b	c	d
Methane	0.105	0.770	1.23	−0.823
Propane	0.148	0.703	0.942	−0.671
Coke gas	0.150	0.695	1.38	−0.707
Hydrogen	0.279	0.680	0.755	−0.393

The initial, or operating, pressure on which the nomographs are based is 1 bara, but they may be used without correction up to a value of 1.2 bara. Data outside this range were not available when the nomographs were formulated, but Bartknecht states that for higher operating pressures it should be assumed that for a given vent area the reduced explosion pressure is proportional to the operating pressure.

An equation equivalent to the Bartknecht nomographs has been given by Simpson (1986). His equation is

$$A_v = aV^b \exp(cP_{stat})P_{red}^d \qquad [17.12.50]$$

where the units are A_v (m^2), P_{red} (barg), P_{stat} (barg) and V (m^3). The range of validity of the equation is

$$1 \le V \le 1000;\ 0.1 \le P_{stat} \le 0.5;\ P_{stat} + 0.1 \le P_{red} \le 2$$

Values of the constants in Equation 17.12.50 are given in Table 17.15. Equation 17.12.50 is quoted in NFPA 68: 1994.

17.12.18 Experimental studies of venting relations

A review of experimental studies comparing the predictions of empirical and semi-empirical equations with experimental results is given by Lunn.

The equations recommended by Lunn as the most versatile are Equation 17.12.11 of Rasbash and Equations 17.12.17 and 17.12.18 of Cubbage and Simmonds. The Runes equation (Equation 17.12.22) contains the constant C, which is too dependent on the particular conditions from which it was derived. The Decker equation (Equation 17.12.19) gives upper limits of P_{red} which are often reasonable but in other cases are overestimates. The Dragosavic equations (Equations 17.12.30 and 17.12.31) are limited to methane–air mixtures, and the Burgoyne and Wilson equation (Equation 17.12.36) to pentane–air mixtures. Rasbash's other equations (Equations 17.12.34 and 17.12.35) are limited to low turbulence, and of the two relations Equation 17.12.34 is superior to Equation 17.12.35 in all cases. The Cubbage and Marshall equation (Equation 17.12.33) is limited to methane–air mixtures as the dependency on the square of the burning velocity tends to give overestimates of P_{red} for gases with high burning velocity.

17.12.19 Modelling of explosion venting

The modelling of combustion in an unvented vessel was described in Section 17.7. Models have also been developed on similar lines for combustion in vented vessels.

17.12.20 Vent outflow equations

The outflow from a vented vessel may be subsonic or sonic. Equations for both types of flow were given in Chapter 15. As the absolute pressure P in the vessel increases relative to atmospheric pressure P_a the ratio w ($=P_a/P$) decreases. When this ratio falls below a critical value w_c ($= 2/(\gamma + 1)^{\gamma/(\gamma+1)}$) sonic flow occurs. The mass outflow per unit area G_v from the vessel is then

$$G_v = C_d f_v \qquad [17.12.51]$$

with

$$f_v = f_{v1} \qquad [17.12.52]$$

$$f_{v1} = f_{vsb1} \quad \text{Subsonic flow} \qquad [17.12.53a]$$

$$= f_{vs1} \quad \text{Sonic flow} \qquad [17.12.53b]$$

$$f_{vsb1} = \left\{ 2P\rho \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_a}{P} \right)^{2/\gamma} - \left(\frac{P_a}{P} \right)^{(\gamma+1)/\gamma} \right] \right\}^{\frac{1}{2}} \quad \text{Subsonic flow} \qquad [17.12.54]$$

$$f_{vs1} = \left[P\rho\gamma \left(\frac{2}{\gamma + 1} \right)^{(\gamma+1)/(\gamma-1)} \right]^{\frac{1}{2}} \quad \text{Sonic flow} \qquad [17.12.55]$$

where C_d is the coefficient of discharge, γ is the ratio of gas specific heats and ρ is the density of the gas. An alternative form of these equations utilized in some models is

$$f_v = (P\rho\gamma)^{\frac{1}{2}} f_{v2} \qquad [17.12.56]$$

$$f_{v2} = f_{vsb2} \quad \text{Subsonic flow} \qquad [17.12.57a]$$

$$= f_{vs2} \quad \text{Sonic flow} \qquad [17.12.57b]$$

with

$$f_{vsb2} = \frac{f_{vbs1}}{(P\rho\gamma)^{\frac{1}{2}}} \quad \text{Subsonic flow} \qquad [17.12.58]$$

$$f_{vs2} = \frac{f_{vs1}}{(P\rho\gamma)^{\frac{1}{2}}} \quad \text{Sonic flow} \qquad [17.12.59]$$

For common gases such as air ($\gamma = 1.4$) the value of w_c is about 0.5.

Two other vent outflow relations which are sometimes used for small pressure drops in the subsonic flow range, for which near-isothermal conditions apply, are

$$f_v = f_{v3} \qquad [17.12.60]$$

or

$$f_v = f_{v4} \qquad [17.12.61]$$

with

$$f_{v3} = [2\rho_o(P - P_a)]^{\frac{1}{2}} \qquad [17.12.62]$$

$$f_{v4} = [2\rho_a P_a \ln(P/P_a)]^{\frac{1}{2}} \qquad [17.12.63]$$

where ρ_a is the density of the gas at atmospheric pressure.

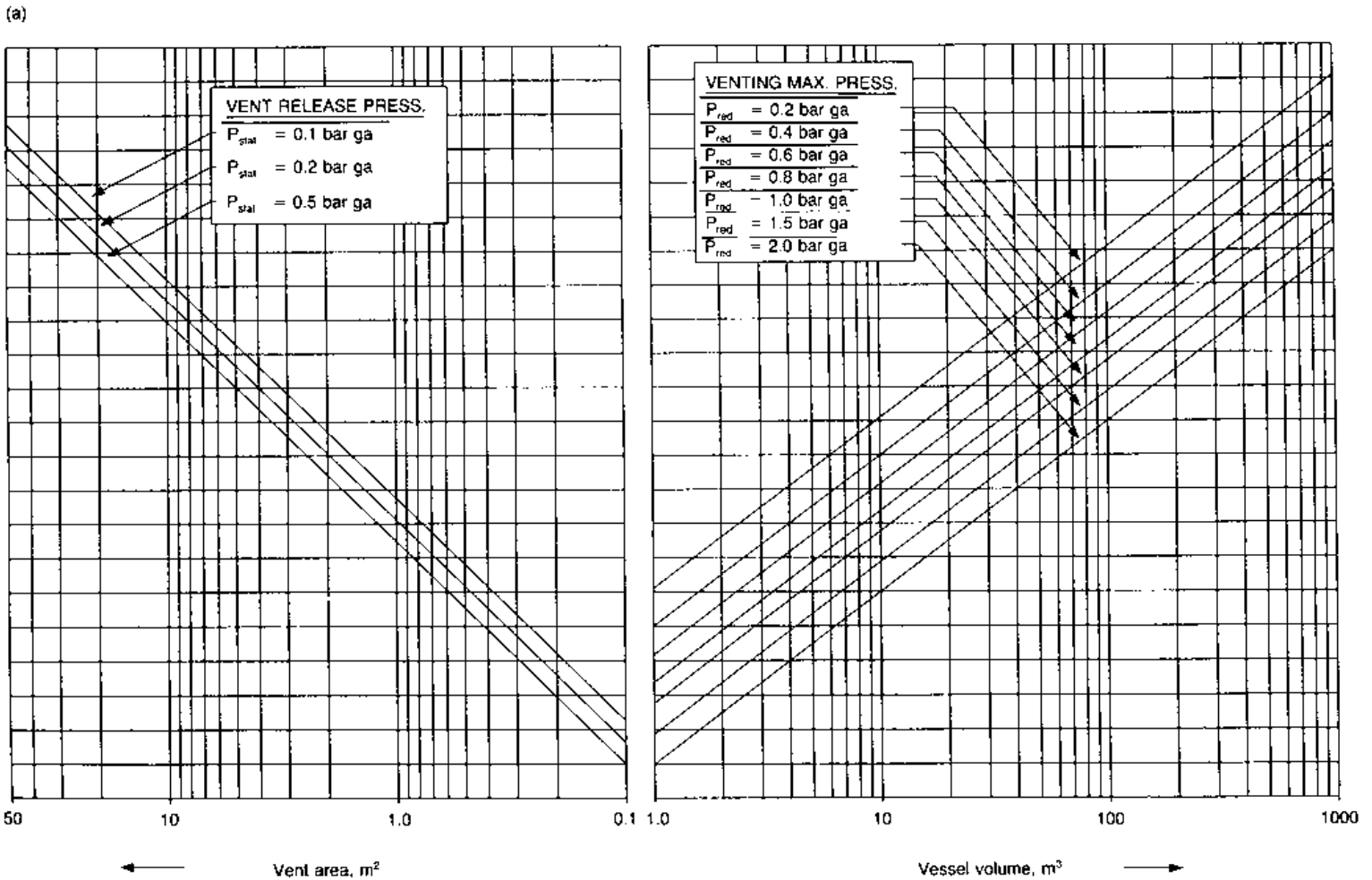

Figure 17.25 *Explosion venting of vessels: nomographs for vent area (NFPA 68: 1994): (a) methane, (b) propane, (c) coke gas and (d) hydrogen. See text for details. (Reproduced with permission from NFPA 68 Deflagration Venting, Copyright © 1994, National Fire Protection Association, Quincy, MA 02269). Note: This reprinted material is not the complete and official position of the National Fire Protection Association on the referenced subject which is represented only by the standard in its entirety)*

(b)

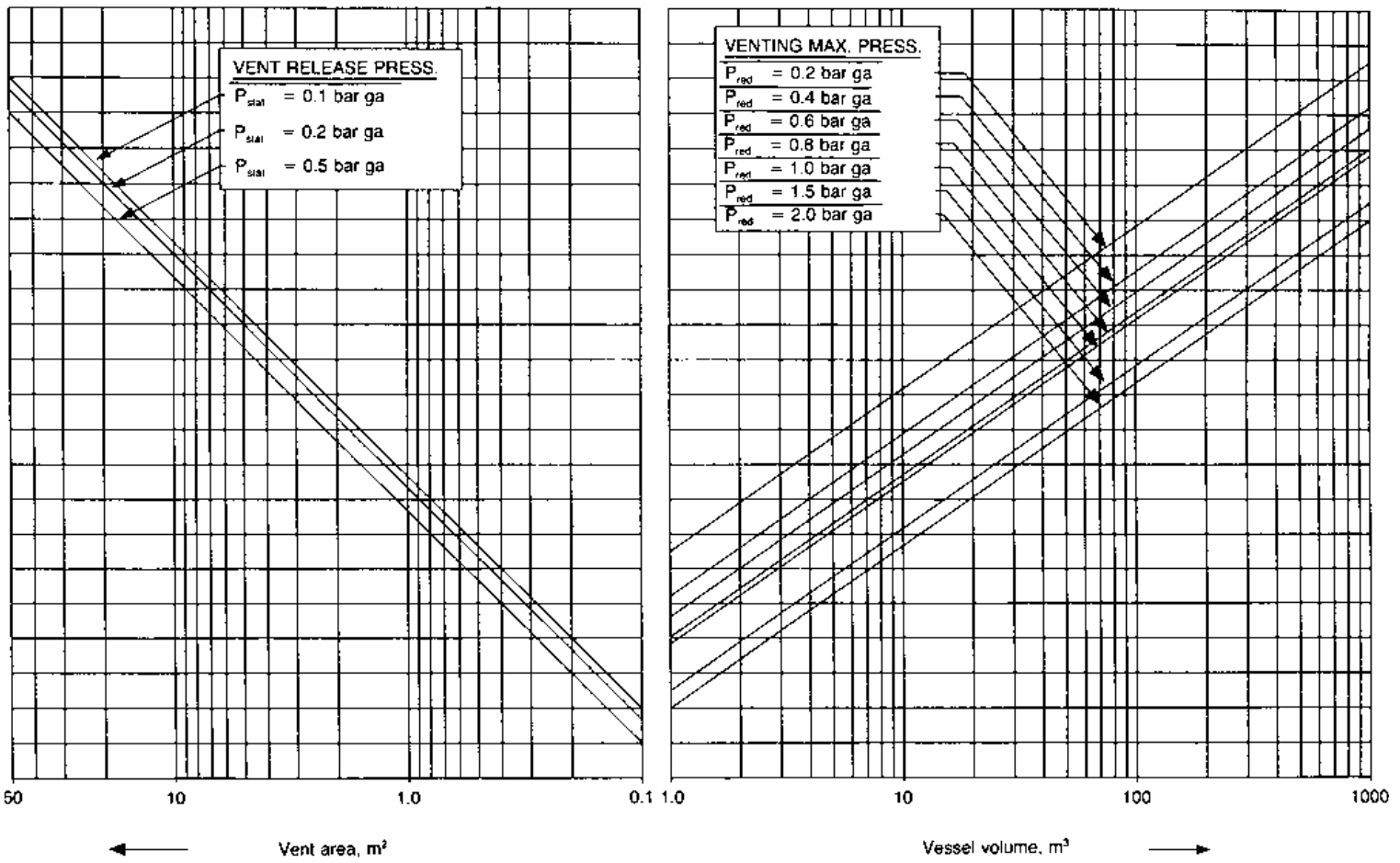

Figure 17.25 *Continued*

(c)

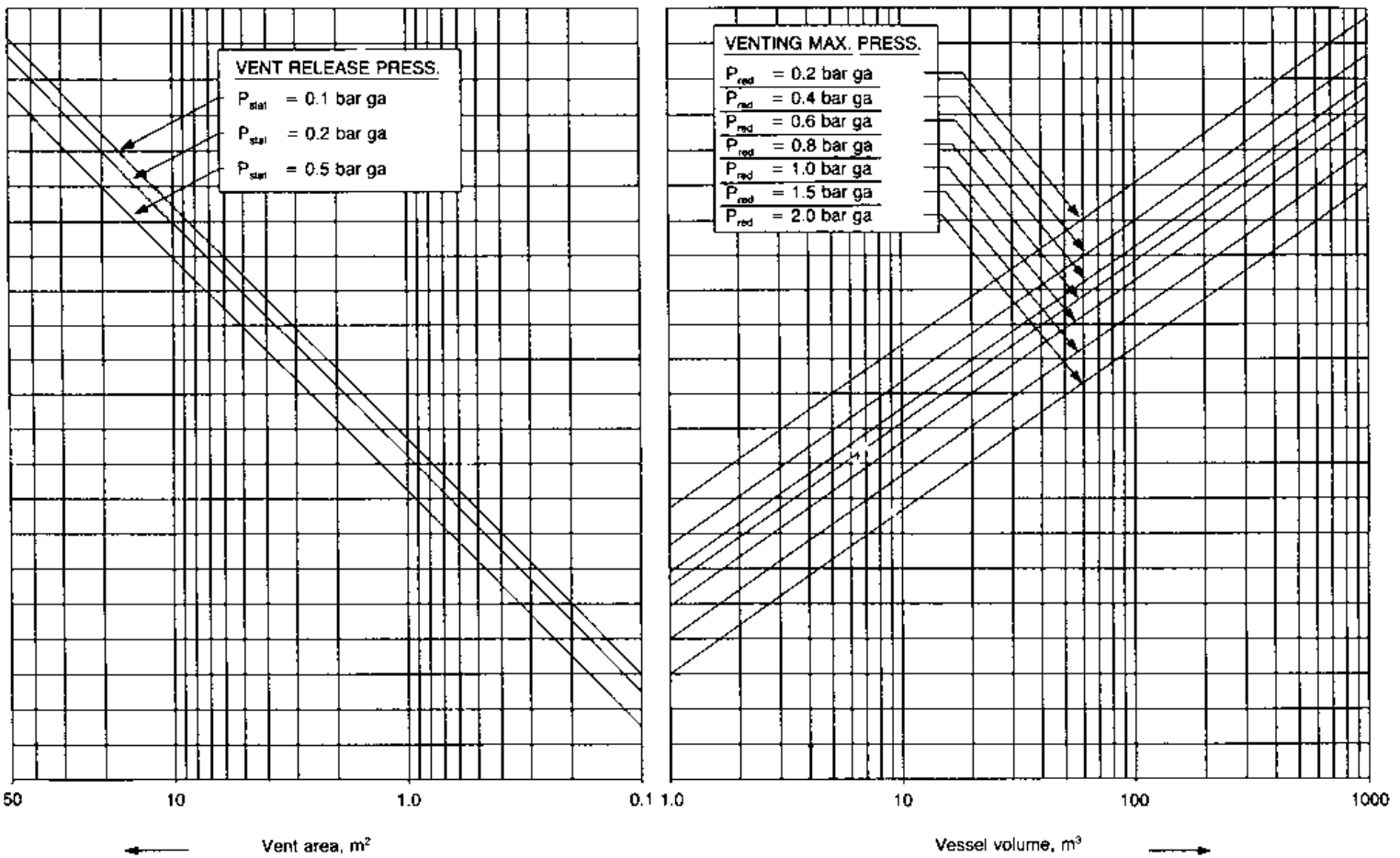

Figure 17.25 *Continued*

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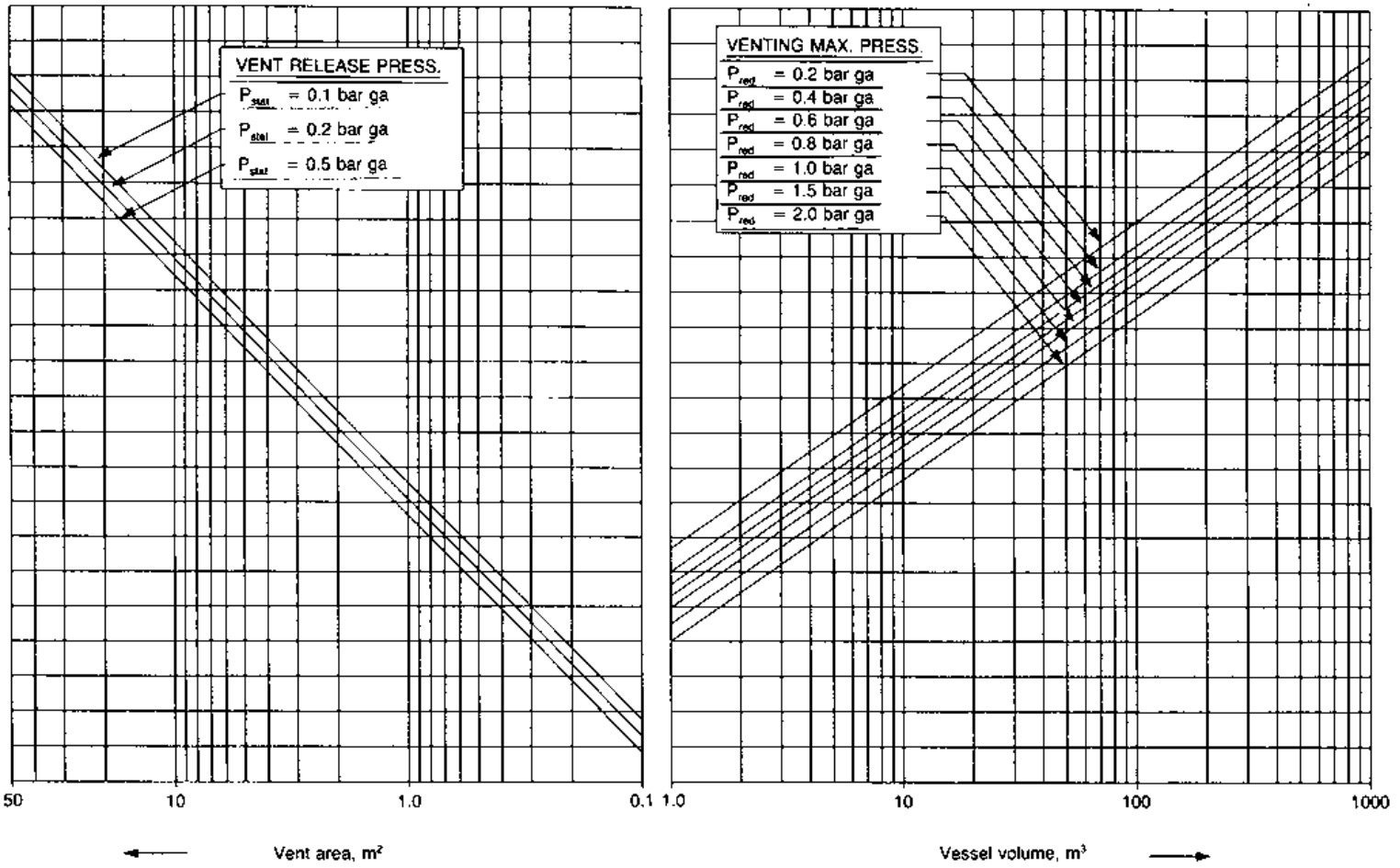


Figure 17.25 *Continued*

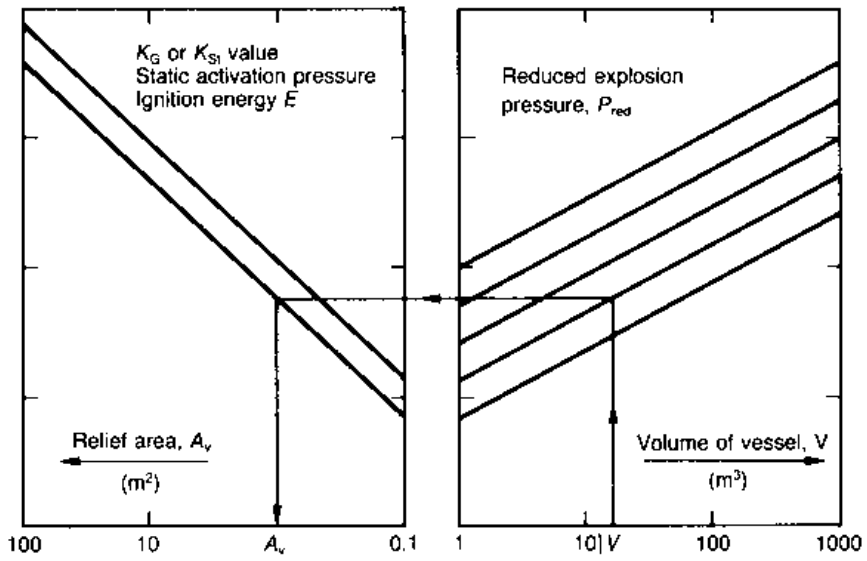


Figure 17.26 *Explosion venting of vessels: nomographs for vent area – use of nomograph (Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

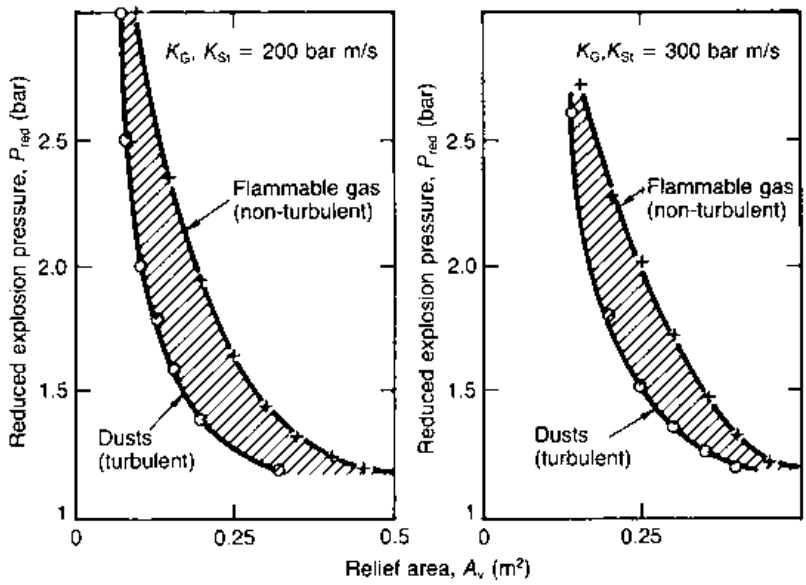


Figure 17.27 *Explosion venting of vessels: vent area recommendations for a 1 m^3 vessel with P_{stat} = 0.1 barg (Bartknecht, 1981a): (a) K_G, K_{St} = 200 bar m/s and (b) K_G, K_{St} = 300 bar m/s (Courtesy of Springer-Verlag)*

17.12.21 Benson and Burgoyne model

In an early treatment of the problem, Benson and Burgoyne (1951) gave the following model for combustion venting of a spherical vessel. From Equation 17.7.15 the rate of increase of the volume V_b of the burned gas expanding as a sphere of radius r_b is

$$\frac{dV_b}{dt} = 4\pi r_b^2 \frac{dr_b}{dt} \quad [17.12.64]$$

The flame speed is

$$\frac{dr_b}{dt} = \frac{EW}{\rho_u} \quad [17.12.65]$$

where E is the expansion ratio defined by Equation 17.7.41, W is the mass rate of combustion and ρ_u the density of the unburned gas. Hence from Equations 17.12.64 and 17.12.65

$$\frac{dV_b}{dt} = \frac{4\pi r_b^2 WE}{\rho_u} \quad [17.12.66]$$

The rate of increase of the burned volume is at a maximum when $r_b = a$, the radius of the vessel, so that

$$\left(\frac{dV_b}{dt}\right)_{max} = \frac{4\pi a^2 WE}{\rho_u} \quad [17.12.67]$$

The volumetric vent flow Q_v at the venting pressure P_{red} through a vent area A_v is

$$Q_v = \frac{C_d A_v f_v}{\rho_u} \quad [17.12.68]$$

Then equating the maximum rate of increase of the burned volume given by Equation 17.12.67 with the volumetric vent outflow in Equation 17.12.68

$$A_v = \frac{4\pi a^2 EW}{C_d f_v} \quad [17.12.69]$$

The density of the unburned gas ρ_u is obtained assuming adiabatic compression:

$$\rho_u = \rho_o \left(\frac{P_{red}}{P_o}\right)^{1/\gamma} \quad [17.12.70]$$

It is pointed out by Lunn that according to Bradley and Mitcheson E in Equation 17.12.65 and the following equations should be replaced by $E - 1$.

17.12.22 Yao model

A numerical model for explosion venting of vessels has been given by Yao and co-workers (Yao *et al.*, 1969; Yao, 1974). The method is intended for venting of low pressure explosions.

The explosions are characterized by a pressure–time profile with two peaks. The model can be made to fit these two peaks fairly well, but to do so requires the use of a turbulence correction factor χ, which allows for effects which enhance the burning velocity or the flame area and is in effect a parameter that can be tuned to fit the experimental results.

Yao (1974) defines a venting parameter α such that

$$\alpha = \frac{(2C_d A_v a)^{\frac{1}{2}}}{S_u V} \left(\frac{P_o}{\rho_{uo}}\right)^{\frac{1}{2}} \left(\frac{\rho_{bo}}{\rho_{uo}}\right)^{\frac{7}{6}} \quad [17.12.71]$$

and a venting area parameter G,

$$G = aA_v/V \quad [17.12.72]$$

where a is a characteristic length (which for a spherical vessel is the radius), ρ_{bo} is the density of the burned gas at the initial pressure and ρ_{uo} is the density of the unburned gas at the initial pressure.

Then for a given maximum explosion pressure ΔP_m

$$\alpha \propto G \quad [17.12.73]$$

and for varying maximum explosion pressure

$$\Delta P_m = f(\alpha) \quad [17.12.74]$$

Yao gives plots of ΔP_m for the second peak as a function of α showing both experimental and theoretical results.

17.12.23 Bradley and Mitcheson method

D. Bradley and Mitcheson (1978) have given two models for combustion venting of a spherical vessel, one an analytical model and the other a numerical, or computer, model. They treat both subsonic and sonic flow and both venting of unburned gas and venting of burned gas.

They define the following parameters:

$$\bar{A} = \frac{C_d A_v}{A_s} \quad [17.12.75]$$

$$\bar{S} = \frac{S_v}{a_v}\left(\frac{\rho_{uv}}{\rho_{bv}} - 1\right) \quad [17.12.76]$$

$$\bar{S}_o = \frac{S_o}{a_{uo}}\left(\frac{\rho_{uo}}{\rho_{bo}} - 1\right) \quad [17.12.77]$$

with

$$a_{uo} = (P_o \gamma_u / \rho_{uo})^{\frac{1}{2}} \quad [17.12.78]$$

where a is the velocity of sound, $\bar{A}$ is the vent area ratio, A_s is the surface area of the spherical vessel, A_v is the vent area, C_d is the coefficient of discharge, P is the pressure, S is the burning velocity, ρ is the gas density, the subscripts b, o, u and v denote burned, initial, unburned and at vent conditions, respectively, and an overbar denotes dimensionless.

The authors state that on the assumption that the initial pressure in the vessel and the external pressure are equal, it can be shown that

$$\frac{\bar{A}}{\bar{S}} \geq f_{v2} \quad [17.12.79]$$

The vent area A_v is that which is just sufficient to vent the volume of gas.

Bradley and Mitcheson give the following volume balance on the gas. The volumetric rate of increase of burned gas is

$$= S_v A_s \frac{\rho_{uv}}{\rho_{bv}} \quad [17.12.80]$$

The volumetric rate of decrease of burned gas is

$$= S_v A_s \quad [17.12.81]$$

Hence the net rate of increase of gas volume is

$$= S_v A_s \left(\frac{\rho_{uv}}{\rho_{bv}} - 1 \right) \quad [17.12.82]$$

The mass rate of venting is

$$\frac{dm_v}{dt} = C_d A_v (P_v \rho_{uv} \gamma)^{\frac{1}{2}} f_{v2} \quad [17.12.83]$$

where m_v the mass vented and P_v the pressure at the vent.

Although not given by Bradley and Mitcheson, the further steps in the derivation are evidently as follows. The volumetric rate of venting is

$$\frac{dV_v}{dt} = C_d A_v \left(\frac{P\gamma}{\rho_{uv}} \right)^{\frac{1}{2}} f_{v2} \quad [17.12.84]$$

where V_v is the volume vented. But

$$\left(\frac{P_v \gamma}{\rho_{uv}} \right)^{\frac{1}{2}} = a_v \quad [17.12.85]$$

where a_v is the velocity of sound at the vent conditions. Then equating the net rate of increase of gas volume given by Equation 17.12.82 with the volumetric rate of venting given by Equation 17.12.84 together with Equation 17.12.85 yields the relation given in Equation 17.12.79 but with an equality.

These authors also give the relation

$$\frac{\bar{A}}{\bar{S}_o} \geq f_{v2} \zeta \quad [17.12.86]$$

with

$$\zeta_u = \frac{S_v(\rho_{uv}/\rho_{bv} - 1)}{S_o(\rho_{uo}/\rho_{bo} - 1)} \left(\frac{P_a}{P_v} \right)^{(\gamma_u - 1)/2\gamma_u} \quad [17.12.87]$$

for the venting of unburned gas and

$$\zeta_b = \zeta_u \left(\frac{\gamma_u}{\gamma_b} \frac{\rho_{bv}}{\rho_{uv}} \right)^{\frac{1}{2}} \quad [17.12.88]$$

for the venting of burned gas, where ζ is the vent flow coefficient. The value of γ in the term f_{v2} in Equation 17.12.86 should also be the appropriate one for unburned or burned gas as the case may be.

17.12.24 Rust model

Rust (1979) has derived the following model for explosion venting of a spherical vessel:

$$V_{fl} = \frac{4}{3} \pi r^3 \quad [17.12.89]$$

with

$$r = ut \quad [17.12.90]$$

and

$$V_t = E V_{fl} \quad [17.12.91]$$

with

$$E = P_{max}/P_o \quad [17.12.92]$$

$$= V_f/V \quad [17.12.93]$$

$$\frac{P}{P_o} = \frac{V_t}{V} \quad [17.12.94]$$

where E is the expansion ratio, P is the absolute pressure, P_{max} is the absolute maximum pressure of the unvented explosion, P_o is the absolute initial pressure, r is the radius of the burned gas before expansion, t is time, u is the velocity of the flame front, V is the volume of the sphere, V_f is the volume of burned gas after expansion at the end of combustion, V_{fl} is the volume of burned gas before expansion and V_t is the volume of burned gas after expansion.

Then from Equations 17.12.89–17.12.92

$$V_t = \frac{4}{3} \pi u^3 t^3 \frac{V_f}{V} \quad [17.12.95]$$

$$= \frac{4}{3} \pi u^3 t^3 \frac{P_{max}}{P_o} \quad [17.12.96]$$

But from Equations 17.12.92, 17.12.93 and 17.12.94

$$\frac{P}{V_t} = \frac{P_{max}}{V_f} \quad [17.12.97]$$

Then from Equations 17.12.95 and 17.12.97

$$P = \frac{4}{3} \pi u^3 t^3 \frac{P_{max}}{V} \quad [17.12.98]$$

Hence

$$P = \frac{Kt^3}{V} \quad [17.12.99]$$

with

$$K = \frac{4}{3} \pi u^3 P_{max} \quad [17.12.100]$$

From Equation 17.12.99

$$t = \frac{(PV)^{\frac{1}{3}}}{K^{\frac{1}{3}}} \quad [17.12.101]$$

and from Equations 17.12.96 and 17.12.100

$$V_t = Kt^3/P_o \quad [17.12.102]$$

Equating the volume production rate dV_t/dt with the vent outflow Q_v

$$Q_v = \frac{dV_t}{dt} \quad [17.12.103]$$

differentiating Equation 17.12.102 with respect to t and substituting for t from Equation 17.12.101 gives

$$Q_v = \frac{3(PV)^{\frac{2}{3}} K^{\frac{1}{3}}}{P_o} \quad [17.12.104]$$

For the volumetric vent outflow Rust uses the relation for subsonic flow

$$Q \propto A_v \, \Delta P^{\frac{1}{2}} \quad [17.12.105]$$

where ΔP is the pressure difference.

Rust sets P in Equation 17.12.104 equal to P_{max} to give a maximum flow requirement and ΔP in Equation 17.12.105 equal to the reduced explosion gauge pressure P_{red} and introduces a shape factor F to take account of non-spherical vessels, defined as

$$F = A_F/A_S \quad [17.12.106]$$

where A_F is the largest spherical surface in the enclosure and A_S the surface area of the sphere having

the same volume as the enclosure. Then from Equations 17.12.104 and 17.12.105 the vent area is

$$A_v = \frac{kF(P_{max}V)^{\frac{2}{3}}K^{\frac{1}{3}}}{P_{red}^{\frac{1}{2}}} \quad [17.12.107]$$

where P_{red} is the reduced pressure (gauge) and k a constant.

In British units, A_v (ft^2), K (lb$_f$ ft/s^3), P_{max} (lb$_f$/ft^2), P_{red} (lb$_f$/ft^2) and V (ft^3), the value of k is 8.35×10^{-5}.

17.12.25 Nagy and Verakis model

Nagy and Verakis (1983) have derived models for the following cases:

(1) venting of cylinder;
  (a) ignition at closed end;
  (b) ignition at vent end;
  (c) ignition in centre;
(5) venting of sphere;
  (a) ignition at centre.

The gas laws are used in the form

$$P_oV = n_oRT_u \quad [17.12.108]$$

$$P_mV = n_oRT_b \quad [17.12.109]$$

$$PV_b = n_bRT_b \quad [17.12.110]$$

$$P(V - V_b) = n_uRT_u \quad [17.12.111]$$

where n is the number of moles (lb mol), P is the absolute pressure (lb$_f$/in.^{2}), R is the universal gas constant (lb ft^3/in.^{2} mol °R), T is the absolute temperature (°R) and V is the volume (ft^3) and the subscripts b, m, o and u denote burned, final, initial and unburned. Also from Equations 17.12.108 and 17.12.109

$$\frac{T_b - T_u}{T_u} = \frac{P_m - P_o}{P_o} \quad [17.12.112]$$

For the vent gas outflow the authors use the following equations:

$$\frac{dn_e}{dt} = \frac{k_{v1}A_v}{T^{\frac{1}{2}}}(P - P_o)^{\frac{1}{2}} \quad \text{Subsonic flow} \quad [17.12.113]$$

and

$$\frac{dn_e}{dt} = \frac{k_{v2}A_v}{T^{\frac{1}{2}}}P \quad \text{Sonic flow} \quad [17.12.114]$$

where A_v is the vent area (ft^2), P_o is the atmospheric pressure (lb$_f$/in.^{2}), k_{v1} (mol in °R$^{\frac{1}{2}}$/lb$^{\frac{1}{2}}$ ft^2 s) and k_{v2} (mol in^2 °R$^{\frac{1}{2}}$/lb ft^2 s) are constants and the subscript e denotes the end of combustion. The values of the constants in these units are $k_{v1} = 20.6$ and $k_{v2} = 2.63$. These values incorporate a mean molecular weight for the vented gas, the value used being that of air ($M = 29$).

The mass balance is

$$\frac{dn_u}{dt} + \frac{dn_b}{dt} + \frac{dn_e}{dt} = 0 \quad [17.12.115]$$

The rate of pressure rise is obtained by differentiating Equations 17.12.110 and 17.12.111 with respect to t and adding them to give

$$\frac{dP}{dt} = \frac{1}{V}\left(\frac{dn_u}{dt}RT_u + \frac{dn_b}{dt}RT_b\right) \quad [17.12.116]$$

Then combining Equations 17.12.115 and 17.12.116 gives

$$\frac{dP}{dt} = \frac{1}{V}\left[\frac{dn_b}{dt}R(T_b - T_u) - \frac{dn_e}{dt}RT_u\right] \quad [17.12.117]$$

The rate of burned gas production is

$$\frac{dn_b}{dt} = \frac{\alpha APS_u}{RT_u} \quad [17.12.118]$$

where A is the area of the flame front (ft^2), S_u is the burning velocity (ft/s) and α is the coefficient of turbulence.

The treatment for the individual cases, which is for an open vent, is then as follows. The case of subsonic flow is considered first.

Venting of cylinder, ignition at closed end

For venting of a cylinder with ignition at the closed end, Equations 17.12.113, 17.12.117 and 17.12.118 yield

$$\frac{dP}{dt} = \frac{\alpha PS_u}{L}\left(\frac{P_m - P_o}{P_o}\right) - \frac{RT_uk_{v1}(A_v/V)}{T_u^{\frac{1}{2}}}(P - P_o)^{\frac{1}{2}} \quad [17.12.119]$$

where L is the length of the cylinder (ft).

Setting $dP/dt = 0$ for the vent condition and also setting P as the vent pressure P_{red} and rearranging gives

$$\frac{P_{red}}{(P_{red} - P_o)^{\frac{1}{2}}} = \frac{RT_uk_{v1}P_oL(A_v/V)}{T_u^{\frac{1}{2}}\alpha S_u(P_m - P_o)} \quad [17.12.120]$$

Equation 17.12.120 is sometimes referred to as the Pittsburgh method. For venting of burned gas the term $T_b^{\frac{1}{2}}$ replaces $T_u^{\frac{1}{2}}$ in the denominator of the term on the right hand side to give

$$\frac{P_{red}}{(P_{red} - P_o)^{\frac{1}{2}}} = \frac{RT_uk_{v1}P_oL(A_v/V)}{T_b^{\frac{1}{2}}\alpha S_u(P_m - P_o)} \quad [17.12.121]$$

Venting of cylinder, ignition at vent end

Venting of a cylinder with ignition at the vent end differs in that burned gas is vented from the start so that

$$\frac{dn_b}{dt} = \frac{\alpha APS_u}{RT_u} - \frac{k_{v1}A_v}{T_b^{\frac{1}{2}}}(P - P_o)^{\frac{1}{2}} \quad [17.12.122a]$$

$$\frac{dn_e}{dt} = \frac{k_{v1}A_v}{T_b^{\frac{1}{2}}}(P - P_o)^{\frac{1}{2}} \quad [17.12.122b]$$

and hence

$$\frac{dP}{dt} = \frac{\alpha PS_u}{L}\left(\frac{P_m - P_o}{P_o}\right) - \frac{RT_bk_{v1}(A_v/V)}{T_b^{\frac{1}{2}}}(P - P_o)^{\frac{1}{2}} \quad [17.12.123]$$

Venting of cylinder, ignition at centre

Venting of a cylinder with ignition at the centre is rather more complex in that there are two flame fronts travelling out from the centre. For the rate of rise of pressure P_1 on the closed end side

$$\frac{dP_1}{dt} = \frac{\alpha P_1 S_u}{L}\left(\frac{P_m - P_o}{P_o}\right) - \frac{RT_u k_{v1}(A_v/V)}{T_u^{\frac{1}{2}}}(P_1 - P_o)^{\frac{1}{2}} \quad [17.12.124]$$

and for the rate of rise of the pressure P_2 on the vent end side

$$\frac{dP_2}{dt} = \frac{\alpha P_2 S_u}{L}\left(\frac{P_m - P_o}{P_o}\right) - \frac{RT_u k_{v1}(A_v/V)}{T_b^{\frac{1}{2}}}(P_2 - P_o)^{\frac{1}{2}} \quad [17.12.125]$$

Summing these two rates of pressure rise gives

$$\frac{dP}{dt} = \frac{2\alpha P S_u}{L}\left(\frac{P_m - P_o}{P_o}\right) - R\left(T_u^{\frac{1}{2}} + \frac{T_u}{T_b^{\frac{1}{2}}}\right)k_{v1}(A_v/V)(P - P_o)^{\frac{1}{2}} \quad [17.12.126]$$

Venting of sphere, ignition at centre

It might be thought that venting of a sphere is a simple case, but this is not so, since the flame front distorts as the gas flows through the vent. The rate of rise of the pressure is considered in two stages. For the period before the burned gas reaches the vent

$$\frac{dP}{dt} = \frac{\alpha P A S_u}{V}\left(\frac{P_m - P_o}{P_o}\right) - \frac{RT_u k_{v1}(A_v/V)}{T_u^{\frac{1}{2}}}(P - P_o)^{\frac{1}{2}} \quad [17.12.127]$$

and for the period after $T_b^{\frac{1}{2}}$ replaces $T_u^{\frac{1}{2}}$ in the denominator of the second term on the right hand side.

The relations for sonic flow may be obtained in a similar manner using Equation 17.12.114.

Summarizing the various cases, Nagy and Verakis state that the most representative relationship for venting is Equation 17.12.121 for the venting of a cylinder with ignition at the closed end. It is that equation which is referred to by Lunn as the Pittsburgh method.

Effect of vent opening pressure

The effect of the vent opening pressure P_v has been allowed for by Nagy and Verakis by modifying Equation 17.12.121 to give

$$\frac{P_{red} + \Delta P_v}{(P_{red} - P_o)^{\frac{1}{2}}} = \frac{RT_u k_{v1} P_o L(A_v/V)}{T_b^{\frac{1}{2}}\alpha S_u (P_m - P_o)} \quad [17.12.128]$$

where ΔP_v is the overpressure at which the vent opens ($lb_f/in.^2$ g)

17.12.26 Singh method

J. Singh (1979b, 1988b) has described a method of vent sizing based on the venting parameter $(\bar{A}/\bar{S}_o)$ of Bradley and Mitcheson described above.

These latter workers defined a maximum pressure rise ΔP_m above the initial pressure and gave a number of plots of ΔP_m vs $(\bar{A}/\bar{S}_o)$. The plot given by Singh is shown in Figure 17.28. The full lines represent sets of data reported by various workers, the dashed lines approximate upper and lower limits on these data. The change of slope in the lines is due to the transition from subsonic to sonic flow as the pressure rises.

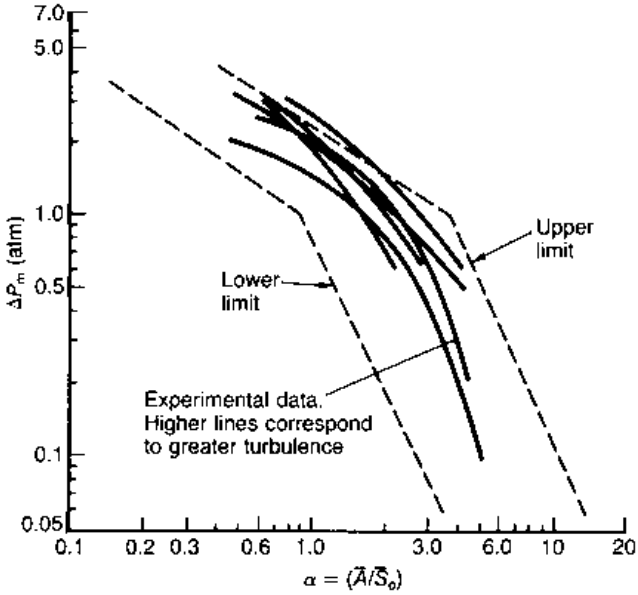


Figure 17.28 *Explosion venting of vessels: effect of normalized vent ratio on maximum pressure rise (J. Singh, 1979b) (Courtesy of Chemical Engineering)*

The equations given by Singh for the two sets of lines are as follows. The basic equation is

$$\Delta P_m = k(\bar{A}/\bar{S}_o)^{-n} \qquad [17.12.129]$$

with for the upper limit lines

$$k = 12.32;\ n = 2 \qquad \Delta P_m \leq 1$$

$$k = 2.4;\ n = 0.7 \qquad \Delta P_m > 1$$

and for the lower limit lines

$$k = 0.77;\ n = 2 \qquad \Delta P_m \leq 1$$

$$k = 0.91;\ n = 0.7 \qquad \Delta P_m > 1$$

where $\bar{A}$ is the dimensionless vent area, ΔP_m is the maximum pressure rise (atm), $\bar{S}_o$ is the dimensionless burning velocity at the initial conditions and k is a constant.

The lower limit lines correspond to situations with essentially zero turbulence. If the burning velocity term in the venting parameter is adjusted to allow for an enhancement of burning velocity by turbulence by a factor of about 4 the upper limit lines are obtained. In other words, the difference in the two sets of lines is mainly due to turbulence.

The burning velocity term of the venting parameter is defined in Equation 17.12.77. The density ratio term may be approximated by the relation

$$\frac{\rho_{uo}}{\rho_{bo}} = \frac{T_{fo}}{T_{uo}} \qquad [17.12.130]$$

where T_f is the adiabatic flame temperature (K), ρ is the density of the gas (kg/m^3) and the subscripts b, o and u denote burned, initial and unburned, respectively. The density ratio tends to lie in the range 7.5–8.5 for most fuels.

J. Singh (1988b) has extended his treatment to non-spherical vessels. From Equation 17.7.137 the rate of pressure rise dP/dt is proportional to the area A_f of the flame front. The following areas apply to different vessel geometries:

$$A_f = 4\pi r_s^2 \quad \text{Sphere} \qquad [17.12.131a]$$

$$= A_s \qquad [17.12.131b]$$

$$A_f = 4\pi r_c^2 \quad \text{Long cylinder with central ignition} \qquad [17.12.132a]$$

$$= 4A_x \qquad [17.12.132b]$$

$$A_f = 2\pi r_c^2 \quad \text{Long cylinder with end ignition} \qquad [17.12.133a]$$

$$= 2A_x \qquad [17.12.133b]$$

where A_f is the area of the flame front (m^2), A_s is the surface area of the sphere (m^2), A_x is the cross-sectional area of the cylinder (m^2), r_c is the radius of the cylinder (m) and r_s is the radius of the sphere (m).

Singh's method is to treat A_s in the venting parameter as equivalent to A_f and to adjust it for non-spherical vessels according to the above relations.

The results of the method are illustrated in Table 17.16.

Table 17.16 *Explosion venting of vessels: overpressures (pressure above vent opening pressure, ΔP_m) in non-spherical vessels using Singh's method (after J. Singh, 1988b) (Courtesy of Butterworth-Heinemann)*

Vent area (m^2)	*Experimental (bar)*	*Theoretical* (bar)	
		Unmodified[a]	*Modified*[b]
0.2	0.048	1.85	0.054
0.1	0.24	3.01	0.22
0.067	0.37	4.0	0.48
0.02	1.22	9.31	1.81

[a] Calculated using Equation 17.12.129, unmodified.
[b] Calculated using Equation 17.12.129, modified by using Equation 17.12.132 or 17.12.133.

17.12.27 Method of Epstein, Swift and Fauske

M. Epstein, Swift and Fauske (1986) have developed a model for explosion venting of a spherical vessel on the following lines. The mass balance is

$$\frac{dm_u}{dt} + \frac{dm_b}{dt} + \frac{dm_e}{dt} = 0 \qquad [17.12.134]$$

The mass production of burned gas is

$$\frac{dm_b}{dt} = 4\pi r_b^2 \rho_u \phi S_u \qquad [17.12.135]$$

and the mass vent outflow is

$$\frac{dm_e}{dt} = A_v G_v \qquad [17.12.136]$$

where ϕ is a turbulence correction factor.

The densities of the unburned and burned gas are

$$\frac{\rho_u}{\rho_{uo}} = \left(\frac{P}{P_o}\right)^{1/\gamma_u} \qquad [17.12.137]$$

$$\frac{\rho_b}{\rho_{bo}} = \left(\frac{P}{P_o}\right)^{1/\gamma_b} \qquad [17.12.138]$$

The volume of the closed vessel is

$$V = \frac{m_u}{\rho_u} + \frac{m_b}{\rho_b} \qquad [17.12.139]$$

Then substituting for ρ_u and ρ_b from Equations 17.12.137 and 17.12.138 in Equation 17.12.139 and then differentiating the latter with respect to t, eliminating dm_u/dt and dm_b/dt using Equations 17.12.135 and 17.12.136, solving for dP/dt, setting $\gamma_u = \gamma_b$ and applying Equation 17.12.139 again yields

$$\frac{V}{\gamma_b}\frac{d\ln P}{dt} = 4\pi r_b^2\left(\frac{\rho_u}{\rho_b} - 1\right)\phi S_u - \frac{A_v G_v}{\rho_u} \qquad [17.12.140]$$

Combining Equations 17.12.135 and 17.12.138, differentiating with respect to time and combining the result with Equation 17.12.140 to eliminate dP/dt yields

$$4\pi r_b^2 \frac{dr_b}{dt} = 4\pi r_b^2\left[\left(\frac{\rho_u}{\rho_b}\right)\phi S_u - \frac{r_b}{3V}\right]\left[4\pi r_b^2\left(\frac{\rho_u}{\rho_b} - 1\right)\phi S_u - \frac{A_v G_u}{\rho_u}\right] \qquad [17.12.141]$$

Dividing Equation 17.12.140 by Equation 17.12.141 gives

$$\frac{1}{\gamma_b}\frac{d\ln P}{dt} = \frac{B(\rho_u/\rho_b - 1)Z^{\frac{2}{3}} - 1}{B[\rho_u/\rho_b - (\rho_u/\rho_b - 1)Z]Z^{\frac{2}{3}} + Z} \quad [17.12.142]$$

with

$$B = \frac{\rho_u \phi S_u A_s}{A_v G_v} \quad [17.12.143]$$

and

$$Z = \frac{4\pi r_b^3}{3V} \quad [17.12.144]$$

where B is a dimensionless burning number and Z a dimensionless burned volume.

For sonic flow Epstein, Swift and Fauske use

$$G_v = (2P\rho_u)^{\frac{1}{2}} \quad [17.12.145]$$

Making a number of additional assumptions the authors derive

$$\frac{P_f}{P_o} = \frac{P_{max}}{P_o}\left(\frac{\lambda + B}{1 + B}\right)^{\gamma_b} \quad [17.12.146]$$

with

$$\lambda = \frac{(P_{set}/P_o)^{1/\gamma_b} - 1}{(P_{max}/P_o)^{1/\gamma_b} - 1} \quad [17.12.147]$$

where P_{set} is the vent opening pressure and λ is a dimensionless vent opening pressure.

The vent area A_v may be obtained from the burning number B defined by Equation 17.12.143.

The model contains a number of approximations. The authors compared their results with results given from the computer model of Bradley and Mitcheson and obtained a good fit, leading them to conclude that the approximations were justified.

This model has been extended by Swift and Epstein (1987) for subsonic flow. For subsonic flow they use

$$G_v = C_d[2P\rho_u(1 - (P_a/P)]^{\frac{1}{2}} \quad [17.12.148]$$

where P_a is atmospheric pressure. They derive an equation equivalent to Equation 17.12.146 for sonic conditions as

$$\frac{P_f}{P_a} = 1 + \left[\left(\frac{P_{max}}{P_o}\right)^{1/\gamma_b} - 1\right]^2 B^2 \quad [17.12.149]$$

where P_f is the absolute final pressure of the vented explosion, or the reduced pressure.

Then rearranging Equation 17.12.149 and substituting for B from Equation 17.12.143 gives

$$A_v = \frac{A_s \rho_u \phi S_u}{C_d G_v}\frac{[(P_{max}/P_o)^{1/\gamma_b} - 1]}{(P_f/P_o - 1)^{\frac{1}{2}}} \quad [17.12.150]$$

17.12.28 Other models

Morton and Nettleton's model for explosion in a closed vessel was described in Section 17.7. The model may be used to determine the vent opening pressure for a given proportion of burned gas in the total gas vented.

As an illustrative example, consider the plot of the pressure ratio P/P_o vs the radius ratio r/a shown in Figure 17.29. From this figure a spherical vessel of 5 m radius with a vent designed to open at 1 barg ($P/P_o = 2$) will have a value of r/a of 0.77. Hence the volume of unburned gas will be 280 m^3 and that of burned gas 240 m^3 at the start of venting.

The model of Fairweather and Vasey (1982) for explosion in a closed vessel was described in Section 17.7. The treatment given by these authors also extends to explosion venting. The mass production of burned gas is given by Equation 17.7.37. The mass vent outflow of gas is obtained from Equation 17.12.51. The mass of unburned gas is given by

$$m_u + m_b = m_o - m_e \quad [17.12.151]$$

The volume of unburned gas is obtained assuming adiabatic compression of the initial gas:

$$V_u = V_o \frac{m_u}{m_o}\left(\frac{P}{P_o}\right)^{-1/\gamma_u} \quad [17.12.152]$$

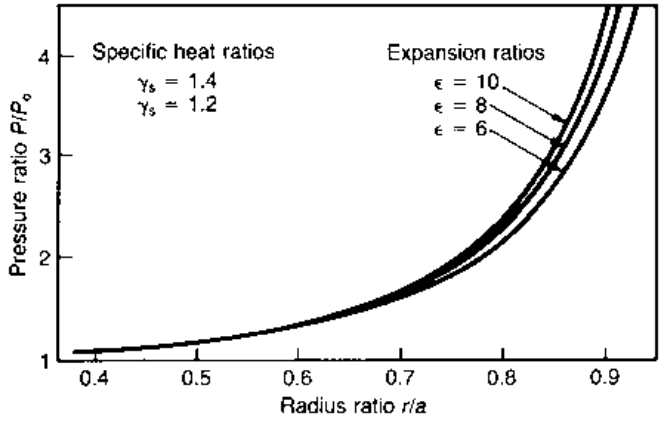


Figure 17.29 *Explosion venting of vessels: variation of pressure with flame radius in a spherical vessel (V.M. Morton and Nettleton, 1977) (Courtesy of the Combustion Institute)*

The volume of burned gas is obtained from Equation 17.7.4. The temperatures of the unburned and burned gases are obtained from Equations 17.7.9, 17.7.10, 17.7.27 and 17.7.28.

17.12.29 Elongated vessels

Vessels which have a length/diameter (L/D) ratio of 3 or less may be regarded as compact, those with an L/D greater than that as elongated.

Another breakpoint occurs at an L/D ratio of 6. The use of a vent area suitable for a vessel with an L/D ratio of 3 or less is usually regarded as conservative for a vessel with an L/D ratio in the range 3–6.

In their early studies of venting, Cousins and Cotton (1951a) investigated a range of L/D ratios from 1.41 to 22.1. The systems which they studied are given in Table 17.14.

They did experiments with 5% propane–air and 40% hydrogen–air mixtures, with open vents and with initial pressures of 0, 15 and 45 psig and measured the maximum pressure of the vented explosion. They expressed their results in terms of plots of this maximum pressure against the vent ratio. Some of the results are shown in Figure 17.30. They show that there is a reasonable correlation with vent ratio across the L/D range investigated.

The work of Singh, described above, also covers elongated vessels with an L/D ratio up to 30.

Further treatment of venting of high L/D containers is given in Section 17.13 on the explosion venting of pipes and ducts.

17.12.30 Critique of available methods

The methods available for the prediction of the vented explosion pressure have been reviewed by Lunn. Of the empirical methods, his preferred methods are those of Cubbage and Simmonds and of Rasbash.

For the Cubbage and Simmonds method to be applicable it is necessary that the vent opening pressure should not exceed 7 kPa and that the vent panel have a low inertia. Then for a vent opening pressure of zero the second peak equation of these authors gives good results. For finite vent opening pressure the results are not so good, since the method does not take vent opening pressure into account.

For finite vent opening pressures up to 7 kPa Lunn states that the first three terms of Rasbash equation give good results for the first peak.

For high vent opening pressures there is no satisfactory method. For this case Lunn recommends the use of the data given by Cousins and Cotton. He also states that the Bartknecht K_G method gives good results.

Lunn states that the methods of Cubbage and Marshall, Runes, Decker, Dragosavic and Burgoyne and Wilson are not recommended for general use.

Of the theoretical methods which he reviews, that of Bradley and Mitcheson gives an upper bound.

17.12.31 Venting phenomena

If the vent is an open one, venting will result in the emergence of flame. The flame may be substantial. C.J.M. van Wingerden (1989c) has reported a jet flame 18 m long.

If the vent has a duct, there is potential for unburned gas to undergo further combustion in the duct, possibly resulting in overpressure in the duct. The ducting needs to be designed to avoid this.

17.12.32 Back reaction due to venting

Venting causes a back reaction on the vessel. The determination of this force may be approached by considering the flow from the vessel or the pressure in the vessel.

A fundamental treatment based on the flow is given by Duncan, Thom and Young (1960). The force is equal to the rate of change of momentum. The mass vent flow from the vessel is $A_v\rho u$, the mass vented in time t is $A_v\rho ut$, its momentum is $A_v\rho u^2t$ and the rate of change of momentum is $A_v\rho u^2$. The resultant force is thus

$$F_r = A_v\rho u^2 \qquad [17.12.153]$$

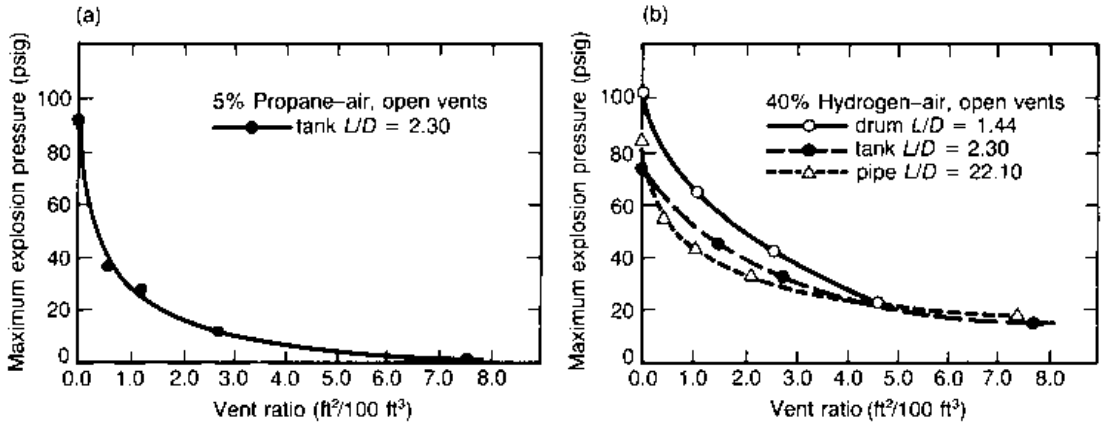


Figure 17.30 *Explosion venting of vessels: effect of vessel aspect ratio on maximum explosion pressure (Cousins and Cotton, 1951a): (a) 5% propane–air mixture in a tank (L/D = 2.30) and (b) 40% hydrogen–air mixture in a drum (L/D = 1.44), tank (L/D = 2.30) and pipe (L/D = 22.1) (Courtesy of* Chemical Engineering*)*

where A_v is the vent area, F_r is the force due to back reaction, t is the time, u is the velocity of the fluid and ρ is the density of the fluid.

Alternatively, the force may be obtained from the pressure P_{red} in the vessel during venting.

The reaction force has also been measured in tests. NFPA 68: 1994 gives the following empirical equation for the reaction force, applicable only to enclosures without ducts:

$$F_r = 1.2 A_v P_{red} \quad [17.12.154]$$

where A_v is the vent area (in.^{2}), F_r is the reaction force (lb_f) and P_{red} is the reduced pressure (gauge) (lb_f/ft^2).

NFPA 68 states that the reaction force can be considered as equivalent to a force applied at the geometric centre of the vent. It warns, however, against assuming that the forces on two opposing vents will cancel out, since one vent may open before the other.

It further states that equivalent static force on the structure supporting the vented enclosure is given by Equation 17.12.154 but with the constant 1.2 replaced by 0.62.

Back reaction forces due to venting are also discussed in Chapter 12.

17.12.33 Vent ducting effects

It has been found that the presence of a vent duct can have a marked effect on the maximum pressure in a vented explosion.

Figure 17.31 is a graph from the work of Pineau, Giltaire and Dangreux (1978), showing the pressure in the vessel and in the duct as function of duct length for a 10 m^3 vented vessel.

Typically the maximum pressure rises rapidly with initial increase in the length of the tube and then reaches a plateau or increases or decreases at a much slower rate. This effect was described by Sagalova and Resnick (1962) for dust explosions and has been observed by Kordylewski and Wach (1986, 1988) for gas.

The latter conducted experiments using a 22 litre vessel with vents and vent tubes of 21, 25 and 35 mm diameter. The gas used was town gas. They were unable to account for the increase in the maximum pressure by the flow resistance of the duct and instead considered turbulence, secondary explosions, acoustic oscillations and Helmholtz oscillations. They found that acoustic oscillations can increase the maximum overpressure by 203 times in tube length in the range 0–20 diameters.

17.12.34 Vent design

Design of a vent system based on a vent panel includes consideration of the following features: (1) reduced explosion pressure, (2) vent opening pressure, (3) vent area, (4) vent distribution, (5) vent opening and (6) vent panel.

The reduced explosion pressure for a vented explosion will be determined by the mechanical strength of the containment. Explosion venting is used for low-strength as well as high-strength equipment.

The vent opening pressure also needs to be set before the vent area can be calculated. The values of the vent opening pressure P_{stat} to which the Bartknecht nomographs apply are $0.1 \leq P_{stat} \leq 0.5$ barg.

The distribution of the vent area determined is generally not critical for vessels, though it may be more important for buildings and modules.

The time of opening of the vent can affect the pressure developed. A sudden opening, such as occurs with a bursting disc, tends to increase turbulence. A smooth opening is desirable to avoid this.

The design of the vent panel itself is important.

17.12.35 Vent panel design

Some features which need to be taken into account in the design of the vent panel itself are (1) panel material, (2) panel inertia, (3) relieving fasteners, (4) panel restraint system, (5) guarding and (6) maintainability.

Detailed guidance on vent panel design is given in the HSE *Guide* and in NFPA 68: 1994.

The guidance given by W.B. Howard and Karabinis (1980) for vent panels for explosion venting of buildings is outlined in Section 17.14.

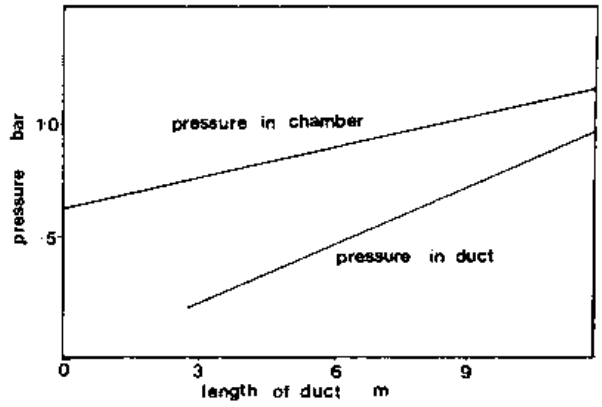


Figure 17.31 *Explosion venting of vessels: effect of vent duct on pressure in a 10 m^3 vessel (Cross and Farrer, 1982; after Pineau, Giltaire and Dangreaux, 1978)*

17.12.36 Vent panel dynamics

The static pressure required to move a vent panel slowly may be quite low, but the pressure needed to impart a high acceleration to the panel so that it moves rapidly may be much higher. Thus

$$F = Ma \qquad [17.12.155]$$

and hence dividing by the area A of the panel

$$P = wa \qquad [17.12.156]$$

with

$$w = M/A \qquad [17.12.157]$$

where a is the acceleration of the panel, F is the force on the panel, M is the mass of the panel, P is the pressure, and w is the inertia of the panel.

An analysis of vent panel dynamics has been given by Rust (1979). He considers the following five situations:

(1) Panel moves by translation; vertical panel; horizontal translation.
(2) Panel moves by translation; horizontal panel; vertical translation.
(3) Panel hinged along width; vertical panel; horizontal rotation.
(4) Panel hinged along width; horizontal panel; vertical rotation against gravity.
(5) Panel hinged along width; horizontal panel; vertical rotation with gravity.

Figure 17.32 illustrates cases (1) and (3).

For a panel of width W and length L which moves by translation a distance S to give a peripheral area WL equal to the vent area A_v, the peripheral area is $2S(W + L)$. Equating these two areas

$$S = \frac{WL}{2(W+L)} \qquad [17.12.158]$$

At pressure P the acceleration a of the panel is

$$a = PA_v/M \qquad [17.12.159]$$

where M is the mass of the panel. From Equations 17.12.99 and 17.12.159

$$a = \frac{Kt^3A_v}{VM} \qquad [17.12.160]$$

Integrating Equation 17.12.160 to obtain the velocity v attained by the panel with the initial condition $t = t_v$, $v = 0$, where t_v is the time of start of venting, and integrating again to obtain the distance s travelled by the panel with the initial condition $t = t_v$, $s = 0$, substituting at $t = t_v$ pressure $P = P_v$, the vent opening pressure, and defining a panel 'density' D,

$$D = Mg/A_v \qquad [17.12.161]$$

where g is the acceleration due to gravity, yields

$$S = g\left(\frac{V}{K}\right)^{\frac{2}{3}}\frac{C}{D} \qquad [17.12.162]$$

with

$$C = \frac{P^{\frac{5}{3}}}{20} - \frac{P_v^{\frac{4}{3}}P^{\frac{1}{3}}}{3} + \frac{P_v^{\frac{5}{3}}}{5} \qquad [17.12.163]$$

where P is the pressure (gauge) (lb_f/ft^2) and P_v is the vent opening pressure (gauge) (lb_f/ft^2).

Relations for the other cases are derived in a similar manner. For cases of rotation, the angle θ to give the vent area is

$$\theta = \frac{W}{W+L} \qquad [17.12.164]$$

and an additional constant E is obtained,

$$E = \frac{P^{\frac{2}{3}}}{2} - P_v^{\frac{1}{3}}P^{\frac{1}{3}} + \frac{P_v^{\frac{2}{3}}}{2} \qquad [17.12.165]$$

Table 17.17 summarizes Rust's equations for vent panel dynamics. In his worked example, in Equations 17.12.163 and 17.12.165 Rust uses a corrected vent opening pressure P'_v ($= P_v + D$), where D is the 'density' of the vent panel (lb/ft^2) and P'_v is the corrected vent opening pressure (gauge) (lb_f/ft^2), instead of P_v.

17.12.37 Vent details

Guidance on details of vents for enclosures, both buildings and equipment, is given in NFPA 68: 1994.

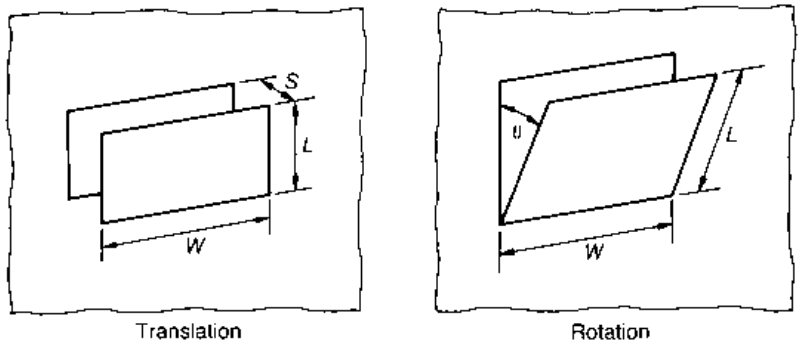


Figure 17.32 *Explosion venting of vessels: movement of vent panels for release of gas (Rust, 1979) (Courtesy of* Chemical Engineering*)*

The vents considered are (1) open or unobstructed vents and (2) closed or sealed vents.

Open vents are applicable to buildings rather than equipment. With a building it is often not practical to have a completely open aperture, but there are various arrangements which can provide good vents. They include louvres, open roof vents and hangar-type doors which can be moved to one side when an operation which may need to be vented is in progress.

Closed vents may be used for either buildings or equipment. Features which can constitute a vent closure for a building or room include a door, window, movable sash, roof or wall panel or skylight. On equipment a vent closure may take the form of a charging door or inspection port, a dedicated venting device or a diaphragm. Diaphragm materials described include paper, cloth, plastic and metal. The diaphragm may be provided with a cutter.

Table 17.17 *Explosion venting of vessels: equations for vent panel dynamics given by Rust (after Rust, 1979) (Courtesy of* Chemical Engineering*)*

Horizontal translation	$S = g\left(\frac{V}{K}\right)^{\frac{2}{3}}\frac{C}{D}$
Horizontal rotation	$\theta = \frac{3g}{2L}\left(\frac{V}{K}\right)^{\frac{2}{3}}\frac{C}{D}$
Vertical translation upward	$S = g\left(\frac{V}{K}\right)^{\frac{2}{3}}\left(\frac{C}{D} - E\right)$
Vertical rotation against gravity	$\theta = \frac{3g}{2L}\left(\frac{V}{K}\right)^{\frac{2}{3}}\left(\frac{C}{D} - E\right)$
Vertical rotation with gravity	$\theta = \frac{3g}{2L}\left(\frac{V}{K}\right)^{\frac{2}{3}}\left(\frac{C}{D} + E\right)$

17.12.38 Vent duct design

The effect of a vent duct on the reduced explosion pressure has already been mentioned. There is available guidance to assist in allowing for this effect.

Correlations due to Bartknecht are shown in Figures 17.33 and 17.34. Figure 17.33, given originally by Bartknecht (1981a) gives the relationship between the reduced explosion pressure with the duct and that without a duct. There are two lines, the parameter being the duct length. Figure 17.34 gives a further correlation for the same relationship, but in this case the parameter is the gas velocity.

Both correlations were given in NPFA 68: 1988, but only the first is retained in NFPA 68: 1994.

17.12.39 Safe discharge

Explosion venting gives rise to three effects: a pressure wave, and discharges of flame and unburned material. All three effects need to be handled safely.

If the material discharged is sufficiently toxic, this may invalidate the venting option.

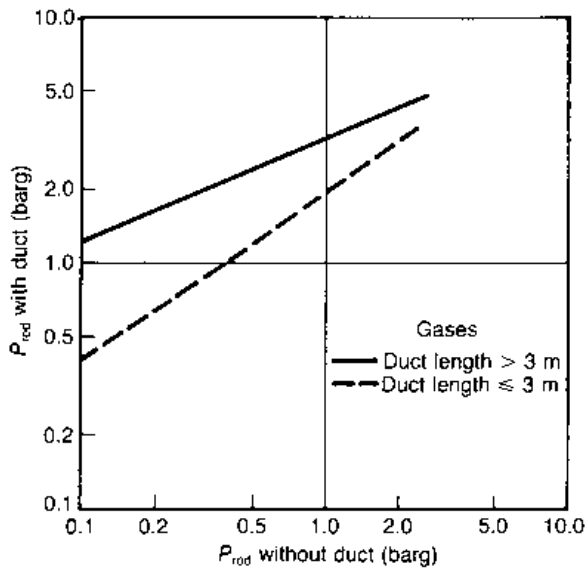


Figure 17.33 *Explosion venting of vessels: effect of length of vent duct on reduced pressure (NFPA 68: 1994). See text for details (Reproduced with permission from NFPA 68 Deflagration Venting, Copyright © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

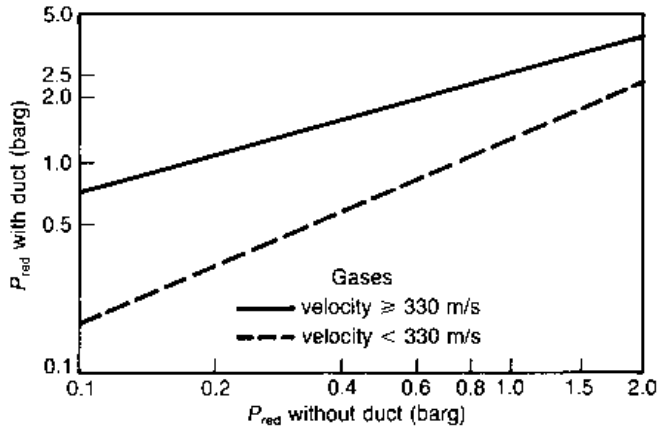


Figure 17.34 *Explosion venting of vessels: effect of velocity in vent duct on reduced pressure (NFPA 68: 1994). See text for details (Reproduced with permission from NFPA 68 Deflagration Venting, copyright © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

17.13 Explosion Venting of Ducts and Pipes

In general, where combustion of a flammable gas mixture occurs in a duct or pipe, there is a possibility that if the duct is long enough the flame front will accelerate to the point where the deflagration turns into a detonation. Detonation is considered in Section 17.6 and is not considered further in this section, which deals with the explosion venting of deflagrations.

The venting of elongated vessels was described in Section 17.12. The methods given there cover the venting of containers with length/diameter (L/D) ratios up to 30.

Accounts of explosion venting of ducts are given in the *Guide to the Use of Flame Arresters and Explosion Reliefs* (HSE, 1965 HSW Bklt 34), *Explosions* (Bartknecht, 1981a), *Venting Gas and Dust Explosions* (Lunn, 1984b), and in NFPA 68: 1994 *Deflagration Venting*.

17.13.1 Experimental studies

The design methods for explosion relief of ducts have tended to draw heavily on experimental work at the Joint Fire Research Organization by Rasbash and Rogowski (Rasbash and Rogowski, 1960a,b; Rogowski and Rasbash, 1963).

The duct dimensions used in the experiments were from 3 in. (76 mm) and 6 in. (152 mm) diameter to 12 in. (305 mm) square section and from 6 to 30 ft (1.8–9 m) long. Most of the experiments were done using propane–air and pentane–air mixtures.

The results of the work are summarized by Lunn (1984b) as follows. For a base case in which a single open vent was located at one end of a straight, unobstructed duct with the ignition source either 15 cm from the closed end or a quarter of the way along the duct and with the most explosive concentration of the gas–air mixture, the vented explosion pressure P_{red} at any position along the duct was proportional to the ratio of the vent area to the cross-sectional area of the duct, or vent coefficient, K, the constant of proportionality ranging from 5.6 to 12.6 for the conditions $6 < L/D < 30$ and $2 < K < 32$. For a vent coefficient K of unity, the maximum explosion pressure P_{max} was proportional to L/D, the constant of proportionality being 0.49 for the conditions $6 < L/D < 48$. The pressure and proportionality constants in the relations just described are in SI units (kPa). Lower vented explosion pressures were obtained when the ignition source was located near the vent or when a given vent area was provided by distributing a number of small vents along the duct.

More recent work is that described by Bartknecht (1981a). The account given by Bartknecht of explosions, both deflagrations and detonations, was summarized in Section 17.5. His recommendations for protection of pipes, which are a combination of containment and relief, are described below.

Work on combustion in pipes has drawn attention to several distinguishing phenomena which are relevant to the design of explosion venting for such systems. If a flammable mixture is ignited in a vessel and then enters an attached pipe, the flame front at the point of entry is fully developed and turbulent. It propagates much more strongly than one arising from spark ignition in the pipe itself.

A flame front travelling down a pipe tends to accelerate, with possible run up to detonation. In addition, turbulence promoters such as bends and valves can cause sudden accelerations of the flame front.

If a flame front travels down an inadequately vented pipe and then enters a vessel containing a flammable mixture, it does so as a jet flame which constitutes a massive ignition source, which can cause a violent explosion in the vessel.

17.13.2 HSE *Guide* method

The methods given in the HSE *Guide* are based on the work of Rasbash and Rogowski just described. Essentially the same methods were used in NFPA 68:

1978, which was superseded by a revision in 1988. Since the methods in the revision of NFPA 68 are a development from this work, although the link is no longer so clear, the HSE *Guide* method is described first.

Unless otherwise stated, HSE *Guide* methods are applicable to gas mixtures at atmospheric pressure. They are applicable to ducts with an L/D ratio of 6 or more. Other methods are available for vessels with an L/D ratio of 3 or less. For containers with an L/D ratio greater than 3 but less than 6 the use of methods for vessels with an L/D ratio of 3 or less is increasingly conservative as the L/D ratio approaches 6.

In designing explosion vents for ducts the following cases are distinguished:

(1) Gas velocity < 10 ft/s –
  (a) straight unobstructed ducts with $L/D < 30$,
  (b) straight unobstructed ducts with $L/D > 30$,
  (c) ducts containing obstacles;
(2) Gas velocity 10–60 ft/s –
  (a) unobstructed ducts,
  (b) ducts containing obstacles.

The design of vent areas is essentially based on the relations between the maximum pressure P and the vent coefficient K.

If the gas is stationery or has a velocity less than 10 ft/s, the duct is straight and unobstructed and the L/D ratio is less than 30, only one relief opening is generally sufficient. The maximum pressure is given by the equation

$$P = k_1 \frac{L}{D} + k_2 K \qquad [17.13.1]$$

where D is the diameter of the duct (ft), K is the ratio of the cross-sectional area of the duct to the vent area, or vent coefficient, L is the length of the duct (ft), P is the maximum pressure ($lb_f/in.^2$) and k_1, k_2 are constants. The values of the constant k_1 and k_2 are:

K	k_1	k_2
1	0.07	0
1–2	0.035	0.9
2–23	0	1.8

If a single vent is used, it should be placed as near as possible to the most probable location of the ignition source, but if this latter is uncertain, the vent should be placed near the centre of the duct.

For this vent system, a vent weighing not more than 2 lb/ft^2 and held by springs or magnets is suitable. An alternative relief is a bursting disc designed to burst at a pressure one half of the maximum pressure given in Equation 17.13.1.

If the gas has a velocity less than 10 ft/s and the duct is straight and unobstructed, but the L/D ratio is greater than 30, it is necessary to have more than one relief opening. The maximum pressure is given by the equation

$$P = k_3 \frac{L_1}{D} + k_4 \qquad [17.13.2]$$

where L_1 is the distance between relief openings (ft) and k_3, k_4 are constants. The values of the constants k_3 and k_4 and the maximum value of the distance between relief openings L_{1max} (ft) are:

K	L_{1max} (diameters)	k_3	k_4
1	60	0.04	0
2	30	0.06	0.1
4	20	0.07	0.2
8	15	0.08	0.3

The open end of a long duct may be regarded as an explosion relief opening. In this context an open end is an end leading without restriction to atmosphere or to a vessel which is itself provided with explosion reliefs or to a room of volume 200 times greater than that of the duct. For such an open end $K = 1$.

If the end of a duct is not open or if it may be regarded as restricted, an explosion relief should be located as near as possible to the end. For this vent system also, vents weighing not more than 2 lb/ft^2 of vent area and held by springs or magnets are suitable.

If at a gas velocity of less than 10 ft/s the duct contains obstacles or features such as sharp right angle elbows or tees, the maximum pressure resulting from an explosion is greatly increased. An obstacle blocking only 5% of the cross-sectional area of the duct can increase the maximum pressure by a factor of 2–3, whilst an orifice blocking 30% of the duct area can increase the pressure by a factor of 10.

Any bend sharper than a long, sweeping, smooth bend and any obstruction blocking more than 5% of the cross-sectional area of the duct should be regarded as an obstacle.

If there is a long straight duct connected to an obstacle, then to reduce the maximum pressure to 2 $lb_f/in.^2$, explosion relief openings of size $K = 1$ should be located as near as possible to the obstacle and at 6 diameters on either side of it. Thereafter the straight unobstructed section of the duct may be treated in the usual way.

For a vent system around an obstacle, a vent weighing not more than 3 lb/ft^2 and held by springs or magnets is suitable.

If the gas has a velocity of 10–60 ft/s and the duct is straight and unobstructed, the explosion relief openings required to limit the maximum pressure resulting from an explosion to 2 lb_f/in^2 are as follows:

D (ft)	L_1/D	K
≤1.5	12	1
	6	2
1.5–2.5	9	1
	5	2

For this vent system, the weight of vents depends on the velocity of the gas. For gas velocities of 25 and of

25–60 ft/s, the vents should weigh not more than 10 and 5 lb/ft^2, respectively. The vents may be held by springs or magnets.

If at a gas velocity of 10–60 ft/s the duct contains obstacles, additional explosion relief openings are required. If there is a long straight duct connected to an obstacle, explosion reliefs of size $K = 1$ should be located at 3 diameters on either side of the obstacle and again at 6 diameters on either side of it. Thereafter the straight unobstructed section of the duct may be treated in the usual way.

For this case, the maximum duct diameter for which information was available is 1.5 ft.

For this vent system, the weight of the six vents nearest the obstacle again depends on the velocity of the gas. For gas velocities below 25 and of 25–60 ft/s, the vents should weigh not more than 3 and 1.5 lb/ft^2, respectively. The vents may be held by springs or magnets.

For gases other than propane, the maximum pressure may be calculated from the maximum pressure for propane using the relation

$$P_2 = \frac{S_u^2}{2.2} P_1 \qquad [17.13.3]$$

where P_1 is the maximum pressure resulting from an explosion for propane (lb$_f$/in^2) P_2 is the maximum pressure resulting from an explosion for a gas other than propane (lb$_f$/in.^{2}) and S_u is the maximum fundamental burning velocity of the gas other than propane (ft/s). The figure of 2.2 derives from the square of the maximum fundamental burning velocity of propane, which is 1.5 ft/s.

Alternatively, for a given maximum pressure the distance between neighbouring vents L_1 may be calculated using the relation

$$L_2 = \frac{2.2}{S_u^2} L_1 \qquad [17.13.4]$$

where L_1 is the distance between relief openings for propane (ft) and L_2 is the distance between relief openings for a gas other than propane (ft).

Vent closures should be designed so that a degree of deterioration or lack of maintenance does not cause the design maximum pressure resulting from the explosion to be exceeded. Closures should be robust and leak-tight. Methods of holding vent closures include springs, magnets and hinges. Further details of vent closure are given in the HSE *Guide*.

It is pointed out by Lunn (1984b) that the experimental data on which these recommendations are based is sparse. He suggests that the maximum pressure correlates as well with vent ratio A_v/V as with vent coefficient K. Figure 17.35 shows the data given by Lunn for vented ducts in support of this argument.

He is also critical of the use of Equation 17.13.3 to extrapolate from propane to other gases. Figure 17.35 shows a curve for the maximum pressure in hydrogen–air mixtures calculated from Equation 17.13.3 which differs appreciably from the experimental curve also shown in the figure.

On the basis of the work of Cousins and Cotton (1951a) he suggests as an alternative that if explosion pressures for a particular gas have been measured in a compact enclosure, then for a duct with $L/D < 30$ and

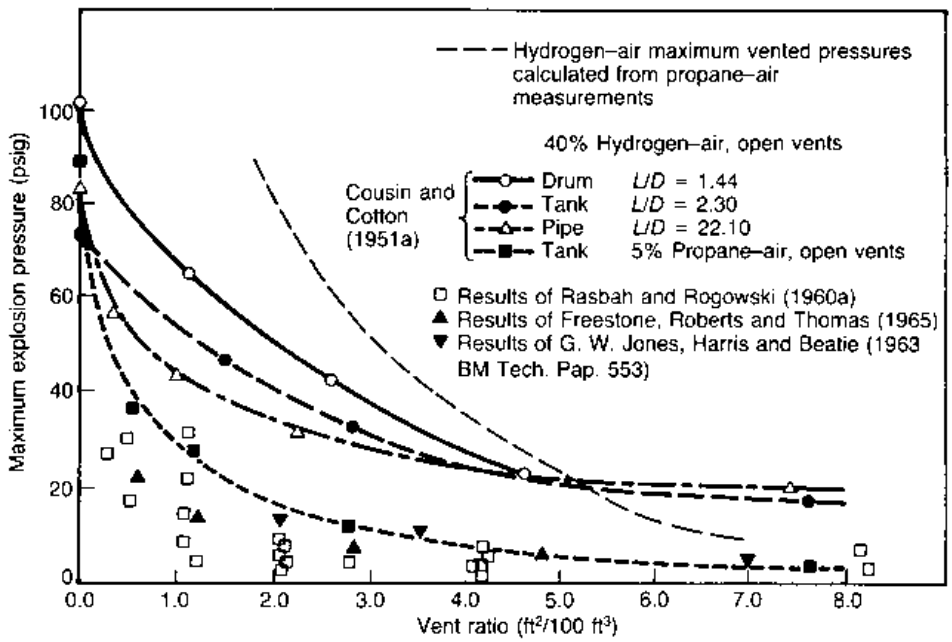


Figure 17.35 *Explosion venting of ducts and pipes: maximum explosion pressure in vessels of different aspect ratios (Lunn, 1984b) (Courtesy of the Institution of Chemical Engineers)*

with the same vent ratio these pressures represent upper bounds on the pressures likely to be occur in the duct.

17.13.3 Bartknecht method

Bartknecht states that experience has shown that explosions may cause considerable damage in pipes even if reliefs are installed.

He suggests that the effectiveness of such reliefs is doubtful, that if they are used they need to be installed every 1–2 m and that such a design is suitable only for use on pipes which are outdoors.

He recommends instead that the pipe should be designed to contain the explosion, which means in practice that it should have a design pressure of at least 10 bar. Such a pipe will withstand even the very high but very short peak pressures associated with detonations.

In this design approach, reliefs are still required but are limited to handling the much higher pressures which occur at end flanges or bends. These must be provided with vents if they are not to be destroyed.

The venting must occur along the axis of the pipe. Relief which is based on flow at right angles to the axis gives much higher pressures for deflagrations and is quite ineffective for detonations. Further, the whole cross-sectional area of the pipe must be utilized for the vent.

As described in Section 17.5, the explosion velocity and explosion pressure developed in a pipe open at one end tend to be higher than in a closed pipe. It follows that if the vent opens too soon, it may aggravate the situation. Therefore, the vent opening pressure should be set sufficiently high to prevent the development of excessive explosion pressure.

One way of achieving this is to use an activated vent in which the explosion pressure is detected by a suitable sensor which causes the vent to open.

Relief devices which can be used include bursting discs and vent doors. The latter have the advantage that they seal the vent opening after effecting relief. However, relief of a pipe is a more demanding duty for a vent door and experience shows that it is not easy to get a suitable design. Many of those tested have either blown off or failed to reseat to give a tight closure.

Another device which might in principle be used is the spring-loaded valve. The explosion pressure forces the valve cover outwards against the force of the springs and the gas vents through the annulus so formed. However, there has been a problem in obtaining a satisfactory design of valve.

17.13.4 NFPA 68 method

As already mentioned, the method of explosion venting for ducts given in NFPA 68: 1988 and 1994 differs from that given in the 1978 edition, which essentially followed the HSE *Guide*.

The method given in NFPA 68: 1994 which is described here is that for the explosion venting of pipes, ducts and elongated vessels operating at or near atmospheric pressure. The pressure is given in the code in terms of the reduced pressure P_{red}, which is expressed as a gauge pressure. The treatment applies to pipes in which the reduced pressure P_{red} is limited to 0.2 barg.

For ducts of non-circular cross-section, the relevant diameter is taken as the hydraulic mean diameter.

Two basic situations are distinguished: (1) a pipe with a single vent consisting of an open end and (2) a pipe with a multiple vents.

NFPA 68 gives several graphs to assist in the design of vents for the relief of deflagrations in pipes. The figures apply to flow in smooth, straight pipes. Some

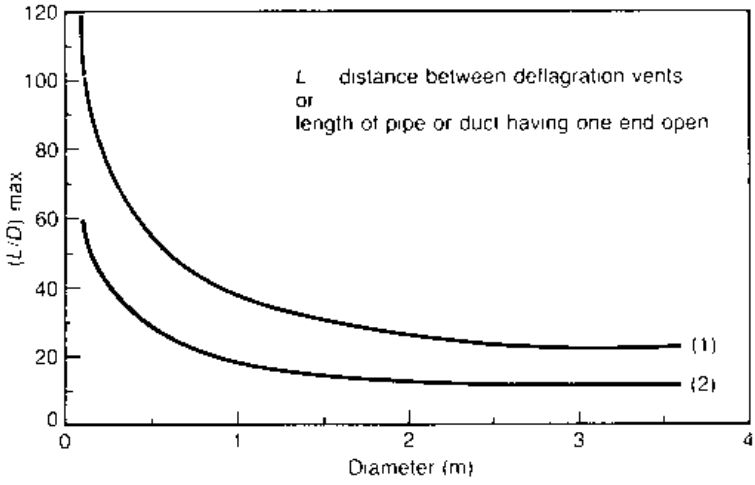


Figure 17.36 *Explosion venting of ducts and pipes: maximum allowable length of a pipe vented at one end, or maximum allowable distance between vents, for gases and dusts (NPFA 68: 1994): (1) dusts with $K_{st} \leq 200$ bar m/s; (2) propane, dust with $K_{st} > 200$ bar m/s. See text for details (Reproduced with permission from NFPA 68 Deflagration Venting, Copyright © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

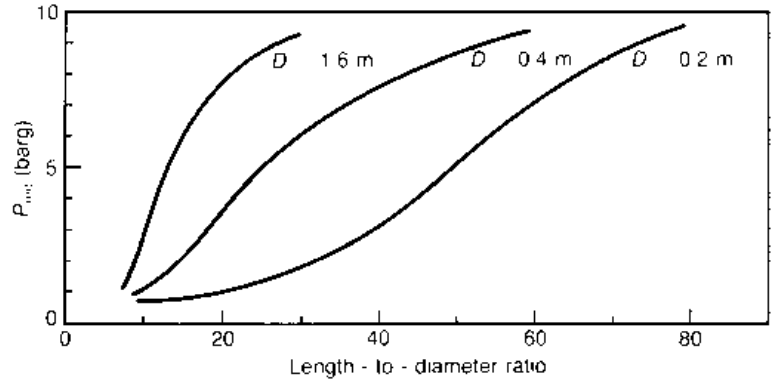


Figure 17.37 *Explosion venting of ducts and pipes: reduced explosion pressure in deflagration of propane–air mixtures in a smooth, straight pipe or duct closed at one end (NPFA 68: 1994). Initial flow velocity <2 m/s. See text for details (Reproduced with permission from NFPA 68 Deflagration Venting, Copyright © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

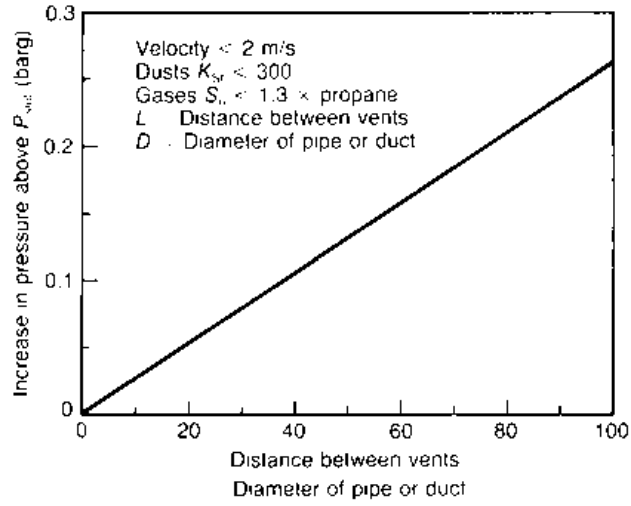


Figure 17.38 *Explosion venting of ducts and pipes: reduced explosion pressure in pipe with multiple vents for deflagration of gases and dusts (NPFA 68: 1994). Initial flow velocity <2 m/s, gas burning velocity ≤1.3 × burning velocity of propane, dust $K_{st} \leq 300$ bar m/s. See text for details (Reproduced with permission from NFPA 68 Deflagration Venting, Copyright © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

are applicable only to propane, but a formula is given which permits them to be applied to certain other gases also, as described below. They are also applicable to dusts, but with restrictions on the St class.

Figure 17.36 is used to determine the maximum allowable length of smooth, straight pipe or vessel which is closed at one end and vented at the other. If the L/D ratio is greater than that shown, there is a risk of detonation. The graph is applicable to propane and to dusts, a distinction being made between dusts with $K_{st} \leq 200$ and $K_{st} > 200$.

Figure 17.37 gives the reduced pressure P_{red} for deflagration of propane in a pipe with a single vent at one end and with an initial velocity <2 m/s.

Figure 17.38 gives the reduced pressure for deflagration of gases and dusts in a pipe with multiple vents for an initial velocity <2 m/s. The limits for gas are a burning velocity ≤1.3 times that of propane and for dusts $K_{st} \leq 300$.

Figure 17.39 gives the spacing of multiple vents for the particular case where, for deflagration of gases and dusts, it is required to limit the reduced pressure to 0.2 barg

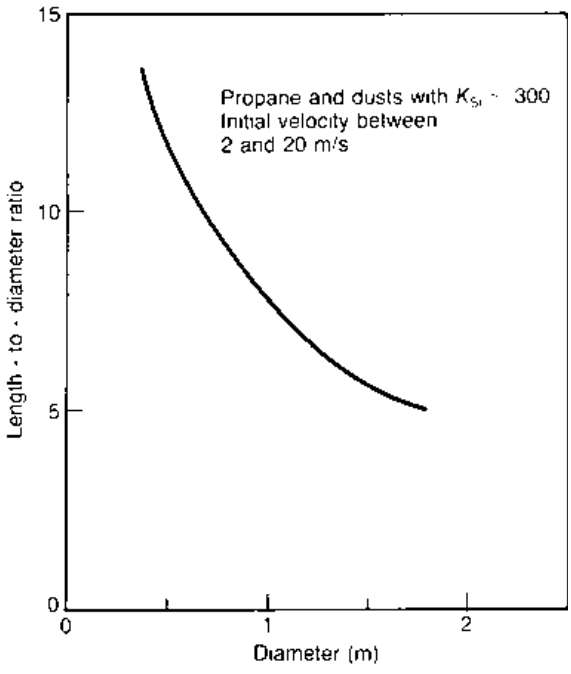


Figure 17.39 *Explosion venting of ducts and pipes: vent spacing to prevent reduced explosion pressure exceeding 0.2 barg for deflagration of gases and dusts (NPFA 68: 1994). Initial flow velocity between 2 and 20 m/s; propane gas, dust $K_{st} \leq 300$ bar m/s. See text for details. (Reproduced with permission from NFPA 68 Deflagration Venting, Copyright © 1994, National Fire Protection Association, Quincy, MA 02269). See note to Figure 17.25*

and where the initial velocity is in the range 2–20 m/s. The limits for gas are a burning velocity $\leq$1.3 times that of propane and for dusts $K_{st} \leq$300.

For gases other than propane which have a burning velocity not exceeding 1.3 times that of propane the following formulae are given:

$$L_x = \left(\frac{S_p}{S_x}\right)^2 L_p \qquad [17.13.5]$$

$$P_{red,x} = \left(\frac{S_x}{S_p}\right)^2 P_{red,p} \qquad [17.13.6]$$

where L is the maximum distance between vents, P_{red} is the reduced pressure, S is the maximum fundamental burning velocity and the subscripts p and x denote propane and the gas in question.

Where the initial velocity exceeds 20 m/s, the gas burning velocity exceeds 1.3 times that of propane or the dust K_{st} value exceeds 300, the distance between vents should not exceed 1–2 m.

Further, for gases, there is additional guidance in respect of obstacles, which include an elbow, tee, flow splitter, orifice or valve, or any feature which blocks more than 5% of the cross-sectional area of the pipe. In such cases in designing for a reduced pressure of $\leq$0.2 barg there should be placed on each side of the obstacle two vents, at distances from the obstacle of 3 and 6 diameters. If the design is for a reduced pressure $>$0.2 barg, it is sufficient to use each side of the obstacle one vent at a distance of 3 diameters from it. The code states that there is insufficient information to allow corresponding guidance to be given for dusts.

With regard to the vents, the total vent area at each location should be at least equal to the cross-sectional area of the pipe. This area may be provided by one or more vents. For an individual vent, an area exceeding the cross-sectional area of the pipe is not effective in further reducing the pressure of a deflagration.

The release pressure of the vents should be set as far below the reduced pressure P_{red} as practical, but in any event should not exceed half the reduced pressure. The mass of the vent closures should not exceed 2.5 lb/ft^2.

NFPA 68 gives a number of worked examples illustrating the application of the above guidance. These include an example involving the specification of the vents on a drier system consisting of the drier itself and a dust collector.

17.14 Explosion Relief of Buildings

An account was given in Section 17.8 of explosions in buildings. In this section explosion relief of such buildings is considered. The relief of dust explosions in buildings is considered in Section 17.48.

Accounts of explosion relief of buildings are given in *Gas Explosions in Buildings and Heating Plants* (R.J. Harris, 1983) and *Venting Gas and Dust Explosions* (Lunn, 1984b) and by Rasbash (1969c), Runes (1972) and W.B. Howard (1972). A relevant code is NPFA 68: 1994 *Deflagration Venting.*

A building is usually too weak to withstand a high explosion pressure and may be blown apart by a sustained pressure of 1 psig (0.07 bar) or even less. Nevertheless, for buildings containing flammable materials it is often appropriate to provide explosion venting. This gives the building a degree of protection against explosions resulting from such causes as leaks and spillages.

Explosion relief of buildings may be regarded as intermediate between explosion relief of vessels and explosion relief of large enclosures such as offshore modules.

17.14.1 Relief by failure of weak components

Most buildings have a number of weaker components such as windows and doors which will fail at a lower pressure than the main structure and to this extent will act as vents.

The designer may take advantage of this fact to provide at least part of the vent area in the form of regular openings with the components deliberately designed to fail at pressures which make them an integral part of the total venting arrangements.

17.14.2 Experimental studies

There have been a number of experimental studies of explosion venting of buildings and large enclosures. Some of the principal studies are listed in Table 17.18.

Table 17.18 *Explosion venting of buildings and modules: some experimental studies*

Investigator(s)	*Vessel or enclosure*			
	Type and dimensions (m)	*Volume* (m^3)	*Relief*	*Gas mixture*
Committee for Explosion Research (1958)	Rectangular enclosure, 8.8 × 5.8 × 3.7–4.15 height	199		
Dragosavic (1973)	Rectangular enclosure, 4 ×3 × 2.6	20.8	Vents	Methane
Solberg, Pappas and Skramstad (1980, 1981)	Rectangular enclosure, 4 × 3.5 × 2.5	35	Open vents	Propane
W.B. Howard and Karabinis (1980)	Rectangular building	81		Propane
Buckland (1980)	Rectangular enclosure, 3.7 × 3.0 × 2.4 height		Vents	Natural gas
A.J. Harrison and Eyre (1986, 1987a,b)	Rectangular enclosure, 5.92 × 2.38 × 2.16	30.4	Open vents?	Natural gas equivalent, propane
C.J.M. van Wingerden (1989c)	Rectangular enclosure, 4.0 × 3.7 × 2.6	38.5	Open vents?	Methane

Reviews on work on explosion relief of buildings have been given by Rasbash (1969c), Butlin (1975 FRS Fire Res. Note 1026) and R.J. Harris (1983).

Early work on explosion relief of a large enclosure of 200 m^3 was carried out by the Committee for Explosion Research (1958) in Sweden. This work is described in Section 17.15. It was particularly valuable in that it was an early contribution and was done on a large scale so that it has provided evidence on scale-up and on phenomena of large scale.

Work at Potters Marston on the characteristics of and damage done by vented explosions in buildings has been described by Astbury *et al.* (1970) and Astbury, West and Hodgkinson (1972, 1973) .

Dragosavic (1972a,b, 1973) has described work at TNO, and has given an equation correlating the results, as described in Section 17.12.

Following an explosion incident in a process plant building, reported earlier by W.B. Howard (1972), explosion relief experiments were performed by W.B. Howard and Karabinis (1980, 1982) on a test building 5.5 × 4.5 × 3 m high. The building contained obstacles to simulate process plant equipment. The tests provided information on potential for structural damage, on explosion venting, and particularly on the Runes constant, and on vent system design.

17.14.3 Empirical and semi-empirical methods

The methods available for the explosion relief of buildings are essentially a subset of those already given for explosion venting of vessels.

Two methods which have been widely used are those of Rasbash (1969c) and Runes (1972). Both methods were in fact developed in the first instance for the relief of buildings.

The methods preferred by R.J. Harris (1983) are those of Cubbage and Simmonds (Cubbage and Simmonds 1955a–c; Simmonds and Cubbage 1960) and of Cubbage and Marshall (1973). Harris gives a theoretical model for the initial rate of pressure rise and initial pressure in an explosion in a building, but not for a vented explosion in a building; for the latter he refers to the model of Fairweather and Vasey (1982). These methods have all been developed by British Gas and thus may be considered to constitute a coherent set of methods for this problem.

17.14.4 Rasbash method

An equation for the maximum pressure in a vented explosion in a building has been given by Rasbash (1969c). This equation has been described in Section 17.12.

In the form given by Rasbash, Drysdale and Kemp (1976) the equation is

$$P_{red} = 1.5P_v + fS_u(P_I + 2.5K)/0.45 \qquad [17.14.1]$$

with

$$P_I = \frac{0.20Kw + 1.17}{V^{\frac{1}{3}}} \qquad [17.14.2]$$

$$K = A_c/A_v \qquad [17.14.3]$$

where A_c is the smallest cross-sectional area of the building space (m^2), A_v is the total area of combustion vents (m^2), f is a turbulence factor, K is the venting ratio, P_I is the back pressure due to inertia of the vent (gauge) (kPa), P_{red} is the maximum pressure reached during the

venting of combustion, or reduced pressure (kPa), P_v is the pressure within the building space at which the vent opens (gauge) (kPa), S_u is the maximum fundamental burning velocity of the gas (m/s), V is the volume of the enclosure (m^3) and w is the inertia of the vent (kg/m^2).

A fuller account of Equation 17.14.1, including details of the parameters and range of validity, is given in Section 17.12.

Equation 17.14.1 has been widely used for the explosion relief of buildings.

17.14.5 Runes method

Another equation which has been widely used for the explosion relief of buildings is that of Runes (1972). This equation also has been described in Section 17.12.

The Runes equation is

$$A_v = \frac{CL_1L_2}{\Delta P^{\frac{1}{2}}} \qquad [17.14.4]$$

with

$$C = \frac{\pi V_f(E-1)}{200} \qquad [17.14.5]$$

where A_v is the vent area (ft^2), E is the expansion ratio, L_1 and L_2 are the two smallest dimensions of the building (ft), ΔP is the vented explosion overpressure ($lb_f/in.^2$), V_f is the flame speed (ft/s), ρ is the density of the gas (lb/ft^3) and C is a constant ($(lb_f/in.^2)^{\frac{1}{2}}$. Runes did not actually give a value of the constant C beyond that which can be calculated for specific cases using Equation 17.14.4.

Runes considered that his equation gives conservative but reasonable vent areas. He presented several worked examples showing that by comparison with the then current version of NFPA 68 his equation gave reasonable values and avoided the more extreme vent areas which the latter sometimes gave. He also gave a comparison with the results of the Bromma explosion venting tests.

Following an explosion incident, W.B. Howard (1972) made proposals for modification of the Runes equation. The explosion occurred in a building which contained process plant equipment and had an area of $5335\,ft^2$ of open windows and of weak components which would act as vents. The end wall was estimated to be able to withstand a static pressure of 7 kPa. This wall was blown off, some portions falling as integral sections, but not forming missiles. Part of the side walls were also blown out and the other end wall was cracked.

Howard first took one of Runes's examples and substituted numerical values to obtain for the case of a gas mixture with a nominal flame speed V_f of 11 ft/s the equation

$$A_v = \frac{1.2L_1L_2}{\Delta P^{\frac{1}{2}}} \qquad [17.14.6]$$

thus giving by comparison with Equation 17.14.4 a Runes constant of 1.2. He substituted the values of A_v and ΔP for the explosion incident, and obtained for the flame speed V_f a value of 24 ft/s. Then taking the ratio of the two flame speeds (24/11) he proposed that the value of the Runes constant be increased to 2.6 ($1.2 \times 24/11$), in effect calibrating the Runes constant from this incident.

In SI units Equation 17.14.4 becomes

$$A_v = C\frac{L_1L_2}{P^{\frac{1}{2}}} \qquad [17.14.7]$$

where A_v is the vent area (m^2), L_1 is the smallest dimension of the rectangular building enclosure to be vented (m), L_2 is the second smallest dimension of that building (m), P is the maximum internal building pressure (kPa) and C is a constant. The maximum internal building pressure P is that which can be withstood by the weakest building member which it is desired should not vent or break.

Equation 17.14.7 is believed to apply to buildings with a nominal length/width, or L/D, ratio up to 3. In a rectangular building where L_1 and L_2 are unequal, D should be taken as $(L_1L_2)^{\frac{1}{2}}$. For a building in which the L/D ratio is greater than 3, the space should be divided into units each of which has an L/D ratio of not more than 3.

The basis of the Runes constant has been explained in Section 17.12. It is discussed by Lunn (1984), who regards it as conservative. The value of the constant was obtained by Howard. The flame speed originally used by Runes was 3.35 m/s for propane–air, whereas that quoted by Howard for ethanol–air is 7.31 m/s, which introduces a factor of 2.2 on Runes' original formulation.

NFPA 68: 1978 gives for C a value in metric units of 6.8 for gases such as propane and others with a similar burning velocity, but a higher value for gases with a higher burning velocity. The suggested value for ethylene is 10.5 and that for hydrogen is 17.

17.14.6 Harris methods

The method used by R.J. Harris (1983) is based on the Cubbage and Simmonds equations given earlier as Equations 17.12.17 and 17.12.18,

$$P_1 = \frac{(4.3Kw + 28)S_u}{V^{\frac{1}{3}}} \qquad [17.14.8]$$

$$P_2 = 58S_uK \qquad [17.14.9]$$

with

$$K = A_s/A_v \qquad [17.14.10]$$

where A_s is the area of the side of the enclosure (m^2), A_v is the vent area (m^2), K is the venting ratio, P_1 is the first peak pressure (mbar), P_2 is the second peak pressure (mbar), S_u is the burning velocity (m/s) and V is the volume of the enclosure (m^3).

Harris also utilizes the Cubbage and Marshall equation given earlier as Equation 17.12.33,

$$P_m = P_v + 23\frac{KwS_u^2}{V^{\frac{1}{3}}} \qquad [17.14.11]$$

with

$$P_v = a/A_v \qquad [17.14.12]$$

where P_m is the maximum pressure reached during venting (mbar), P_v is the pressure at which the vent opens (mbar), S_u is the maximum fundamental burning velocity of the gas (m/s), and w is the inertia of the vent (kg/m^2). The constant a is numerically equivalent to the failure pressure of a panel of unit area.

As an illustration of the use of these two equations, Harris gives the example of the calculation of the

explosion relief for a furnace $5 \times 5 \times 5$ m fired by natural gas with a limit of $3\,m^2$ on the size of any one vent panel. The maximum pressure rise is to be limited to 250 mbar, and the panel inertia is $10\,kg/m^2$. The burning velocity is taken as 0.45 m/s, the turbulence factor as 3, and the constant a is 40.

Then by the method of Cubbage and Simmonds taking the maximum pressure as that occurring in the second pressure peak as given by Equation 17.14.9

$$A_v = \frac{58 \times (3 \times 0.45) \times 5^2}{250}$$

$$= 7.83\ m^2$$

$$K = 5^2/7.83$$

$$= 3.2$$

This indicates the need for three panels.

For the method of Cubbage and Marshall, Harris recast Equation 17.14.11 in the following forms. For a relief panel in the side with the largest cross-section:

$$A_v = \frac{1}{P_m}[a + 23A_s w S_u^2/V^{1/3}]; \quad K = \frac{A_s}{A_v}$$

and for panels on any other side

$$A_v = \frac{1}{P_m}[a + 23V^{1/3} w S_u^2]; \quad K = \frac{V^{2/3}}{A_v}$$

$$A_v = \frac{1}{250}[40 + 23 \times (5^3)^{1/3} \times 10 \times (3 \times 0.45)^2] = 8.5$$

$$K = (5^3)^{2/3}/8.5 = 2.9$$

This again indicates the need for three panels.

17.14.7 NPFA 68 method

Explosion relief of buildings is treated in NFPA 68: 1994. The approach adopted has evolved over the years. That used in the 1974 edition was to calculate the vent area A_v using both the Rasbash and the Runes equations and to take the larger of the two areas. The 1978 edition gave only the Runes equation.

For the venting of low strength enclosures, including buildings, NFPA 68: 1994 gives the following equation:

$$A_v = C\frac{A_s}{P_{red}^{\frac{1}{2}}} \qquad P_{red} \leq 0.1 \qquad [17.14.13]$$

where A_s is the internal surface area of the enclosure (m^2), A_v is the vent area (m^2), P_{red} is the maximum internal overpresssure which can be withstood by the weakest structural element not intended to fail (bar) and C is a venting constant ($bar^{\frac{1}{2}}$).

For the venting constant the code gives in metric units a value of $0.045\,bar^{\frac{1}{2}}$ for gases which have a fundamental burning velocity less than 1.3 times that of propane. The value of the constant for methane is $0.037\,bar^{\frac{1}{2}}$.

NFPA 68: 1994 gives an illustrative example of the use of Equation 17.14.13 involving a building of fairly complex shape.

17.14.8 Relief of multiple compartments

It can occur that the leak of flammable gas enters more than one compartment of the building and that an explosion in one compartment may propagate to another. An event in which explosions propagate in this way is known as a cascade explosion.

There are several factors which may cause the pressure in the second compartment to be higher than that in the first. The explosion in the first compartment may cause compression of, and turbulence in, the gas in the second compartment.

Cubbage and Marshall (1973) performed experiments using two interconnected rooms each of which had a volume of $28\,m^3$. They derived the following equation for the vented explosion pressure P_2 in the second compartment following ignition:

$$P_2 = (k_1 P_1 + k_2 P_1^2)^{0.5} \qquad [17.14.14]$$

with

$$k_1 = \frac{V_2}{V_1}\left(46(Kw)_{2av}\frac{S_u^2}{V_2^{0.33}}\right) \qquad [17.14.15]$$

$$k_2 = \frac{V_2}{V_1}\frac{K_2}{K_{12}} \qquad [17.14.16]$$

where K_1, K_{12} and K_2 are the vent coefficients for compartment 1, between compartments 1 and 2 and for compartment 2, $(Kw)_{2av}$ is the average value of Kw for compartment 2, P_1 and P_2 are the vented explosion pressures of compartment 1 and of compartment 2 (mbar), and V_1 and V_2 are the volumes of compartment 1 and of compartment 2 (m^3), respectively, and k_1, k_2 are constants.

The experiments were done with large vent openings. It is uncertain how far the results can be extrapolated. Harris recommends against their general use.

17.14.9 Vent design

It is preferable that the vent areas should be located on different walls of the building rather than concentrated all on one wall.

Vent panels for buildings should have the lowest practicable inertia. The release pressure for a vent panel should be as low as possible relative to the expected wind pressures. An appropriate value is usually in the range 1–1.5 kPa.

A vent panel should be restrained by a device such as a hinge or chain to prevent it flying off the building if it does open. Consideration should be given to the space into which the panel is to open.

Materials which shatter into pointed fragments should not be used for vent panels. In particular, asbestos cement-type board is unsuitable.

It may be necessary to provide railings along the edge of the floor near a vent panel to prevent people accidentally knocking the panel open and falling out.

An account of the guidance in NFPA 68 on design of vents for enclosures generally, including buildings, has been given in Section 17.12.

17.15 Explosion Relief of Large Enclosures

An account was given in Section 17.9 of explosion in a large enclosure such as an offshore module. In this

section explosion relief of such an enclosure is considered.

17.15.1 Relief by structural collapse

Explosion relief of a large enclosure may occur in two ways. The relief may take place exclusively through vent apertures which already exist and which are intended as vents or it may also take place through apertures which are created by the explosion itself. In the latter case the extent of the relief opening will depend on the degree of structural collapse and hence on the strength of the explosion.

Such relief may be investigated using one of the computer codes for simulation of a semi-confined explosion. In this case it will usually be necessary to adopt an iterative procedure, calculating initially the strength of the explosion without structural collapse, determining the degree of collapse for this maximum strength explosion, and gradually adjusting the strength of the explosion and the degree of structural collapse until a match is obtained.

17.15.2 Experimental studies

Experiments on large vented explosions using a steel module of dimension $2.5 \times 3.5 \times 4\,\text{m}$, and hence $35\,\text{m}^3$ volume, were performed by Solberg, Pappas and Skramstad (1981). Vent openings extended all the way along the front wall and could be varied in steps of $0.25\,\text{m}^2$. A propane–air mixture was used.

Tests were done with the ignition source at three different locations: at the centre of the module, at the vent opening and at the rear wall. In all cases the overpressure gave two peaks. Typical overpressure traces are shown in Figure 17.40.

With central ignition the overpressure rose until the hot burned gas began to flow through the vent. The volumetric flow then increased, the density of the gas being less. The pressure rise was arrested. This effect also inhibited the backward propagation of the flame front towards the rear wall. The arrest of this flame front created just the conditions which favour Taylor instability. Under these conditions the flame front breaks up into a large number of fronts propagating in many directions. There is a massive increase in the rate of combustion and a large increase in the overpressure. This is illustrated in Figure 17.41.

This phenomenon was not limited to the case of central ignition. It occurred with ignition at the vent opening also. For Taylor instability a major part of the flame must be able to propagate away from the vent opening, but the distance between the ignition source and the opening is not important.

With the ignition source at the rear wall the course of the explosion was different. In this case there was less scope for Taylor instability. However, there was still a strong second peak. This was thought to be due probably to the shear between the high velocity burned gas and the low velocity unburned gas and consequent enhancement of turbulence at the flame front. This is illustrated in Figure 17.42.

The authors also explored the validity of vent coefficient scaling ($A_v/V^{\frac{2}{3}} = \text{constant}$). They found that for large volumes such scaling was not valid and was not conservative. They concluded that whereas combustion in small volumes is characterized by a small, spherical

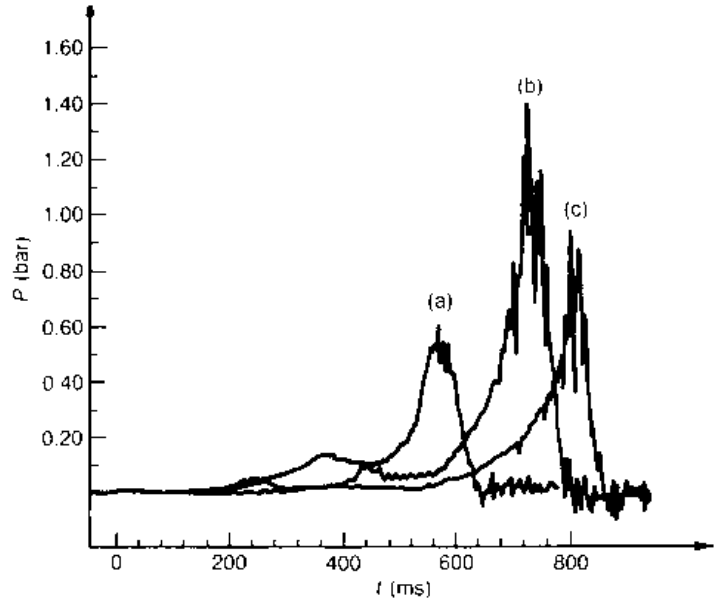


Figure 17.40 *Explosion venting of large enclosures: profiles of overpressure for explosions with different locations of the ignition source – 1: (a) rear wall ignition, (b) central ignition and (c) front wall ignition (Solberg, Pappas and Skramstad, 1981) P, pressure; t, time (Courtesy of the Combustion Institute)*

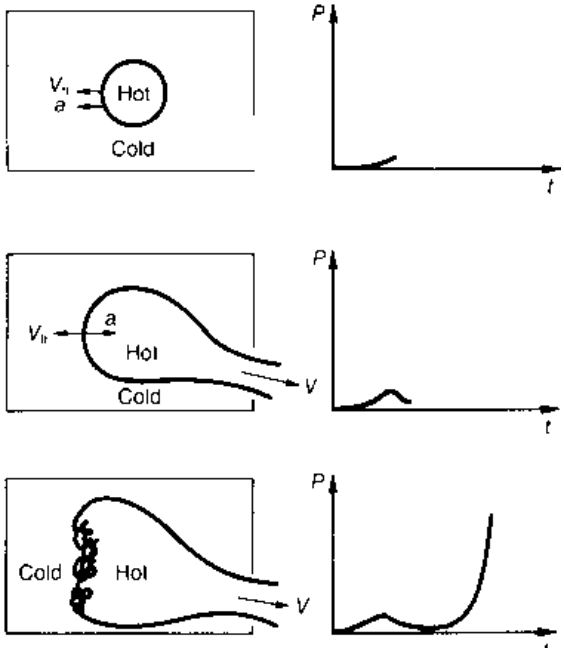


Figure 17.41 *Explosion venting of large enclosures: development of a vented explosion with central ignition showing Taylor instability (schematic) (Solberg, Pappas and Skramstad, 1981) P, pressure; t, time (Courtesy of the Combustion Institute)*

flame front, in larger volumes combustion instabilities dominate.

Experiments on generation of overpressures in vapour clouds have been described by A.J. Harrison and Eyre (1986, 1987a,b). This work included investigation of the ignition of a vapour cloud by a jet flame issuing from a vented chamber. In this work it was observed that when unburned gas displaced from the chamber was ignited by the emerging flame, there occurred a rapid combustion of the displaced gas, near spherical in form and located a few metres from the vent opening. They termed this an 'external explosion'. They noted that a similar phenomenon had been reported by Solberg, Pappas and Skramstad (1980).

Overpressure traces showing the external explosion are given in Figure 17.43. Figure 17.43(a) shows the overpressure at the rear wall of the chamber and Figure 17.43(b) that just outside the chamber. The peak caused by the external explosion occurs first.

The blast wave from the external explosion is shown in Figure 17.44. The overpressure is constant for some distance from the vent opening to a virtual centre and then falls off, the decay being proportional to the reciprocal of the distance from that centre.

C.J.M. van Wingerden (1989c) has reported experiments to investigate the various effects which may enhance the overpressures obtained in large vented explosions. He lists as possible enhancing mechanisms shear turbulence, oscillatory combustion and Taylor instability.

The tests were performed using a chamber 2.6 × 3.7 × 4.0 m, and hence volume 38.5 m^3, and methane–air mixtures. Features investigated included vent area, vent shape, ignition source location, effect of an obstacle and gas concentration.

The overpressure traces obtained had two peaks. Van Wingerden attributes the first to opening of the vent cover and the second, which was generally larger than the first, to oscillatory combustion. An acoustic wave generated during the combustion process enhances combustion and creates higher overpressures. A frequency analysis showed a maximum at a frequency of 120 Hz, corresponding to the fundamental mode of the chamber with the wave standing between the two side walls. The repeatability of this mechanism was low, however, and the overpressures obtained varied by a factor of nearly two.

An external explosion occurred and had the effect of making the pressure peaks rather sharp.

Overpressures measured with vent areas $\leq 5.2\,m^2$ were low, but high overpressures were obtained with vent areas $>5.2\,m^2$. No explanation was found for this anomalous effect. Vent shape and vent opening pressure had little effect. There was a wide scatter of overpressures for different vent opening pressures.

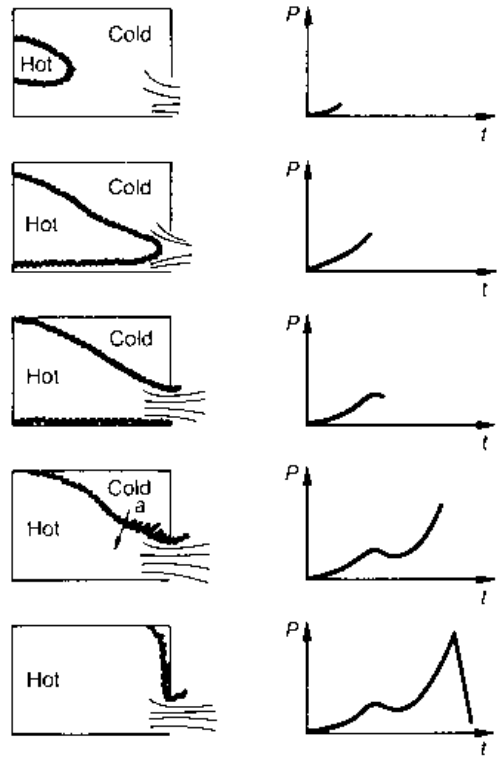


Figure 17.42 *Explosion venting of large enclosures: development of a vented explosion with rear wall ignition (schematic) (Solberg, Pappas and Skramstad, 1981) P, pressure; t, time (Courtesy of the Combustion Institute)*

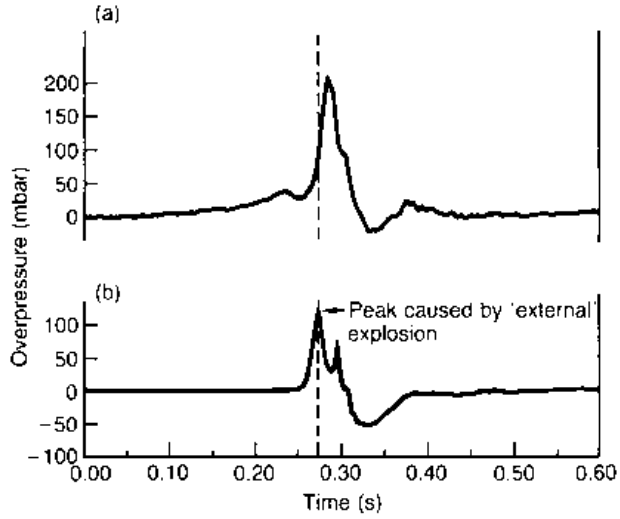


Figure 17.43 *Explosion venting of large enclosures: profiles of overpressure inside and outside the enclosure showing effect of external explosion: (a) overpressure at rear wall; and (b) overpressure just outside enclosure (A.J. Harrison and Eyre, 1986; reproduced with permission)*

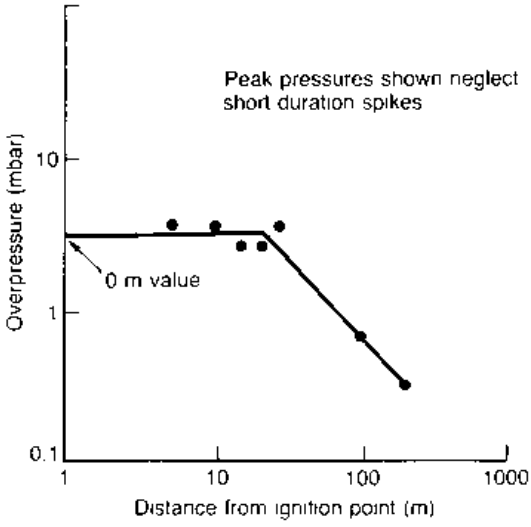


Figure 17.44 *Explosion venting of large enclosures: decay of overpressure outside enclosure (A.J. Harrison and Eyre, 1987a) (Courtesy of Combustion Science and Technology)*

The location of the ignition source affected the overpressure traces obtained but had little influence on the maximum overpressures obtained. Central ignition and ignition at the vent opening gave a maximum overpressure due to oscillatory combustion, whilst rear wall ignition gave a maximum overpressure due to the external explosion.

Tests were done with a single obstacle which, depending on its orientation blocked 12 or 23% of the cross-section of the chamber. With this configuration, overpressure traces with three peaks were obtained. Van Wingerden attributes the first to the opening of the vent, the third to oscillatory combustion and the second to turbulent combustion in the wake of the obstacle proceeding outside the enclosure. This second peak increased as the distance between the ignition source and the obstacle increased. The peak was at a maximum when this distance was large.

Gas concentrations used were 9.5 and 10% methane–air mixtures. Oscillatory behaviour was obtained more readily with the latter and this was used in most of the work.

The venting of the explosion gave rise to long flame jets, up to 18 m in length.

The overpressure due to the blast wave outside the chamber was also measured. There were two pressure peaks, the first due to the external explosion and the second due to the internal explosion. With central ignition the two peaks were comparable, whilst with rear wall ignition that due to the external explosion was dominant. Essentially the strength of the blast wave depended on the external explosion. The overpressure was constant for some distance from the vent opening and then decayed inversely with the distance.

A review of the experimental evidence on the overpressures which might occur due to an explosion in a vented module was given to the Piper Alpha Inquiry by Chamberlain (1989). He drew attention to the complexity of the phenomena involved and illustrated this by reference to the overpressure traces shown in Figure 17.45. Figure 17.45(a) is for a case with central ignition and exhibits five peaks: peak 1 at vent panel rupture, peak 2 at flame emergence from the vent, peak 3 at the moment of external explosion, peak 4 due to Helmholtz

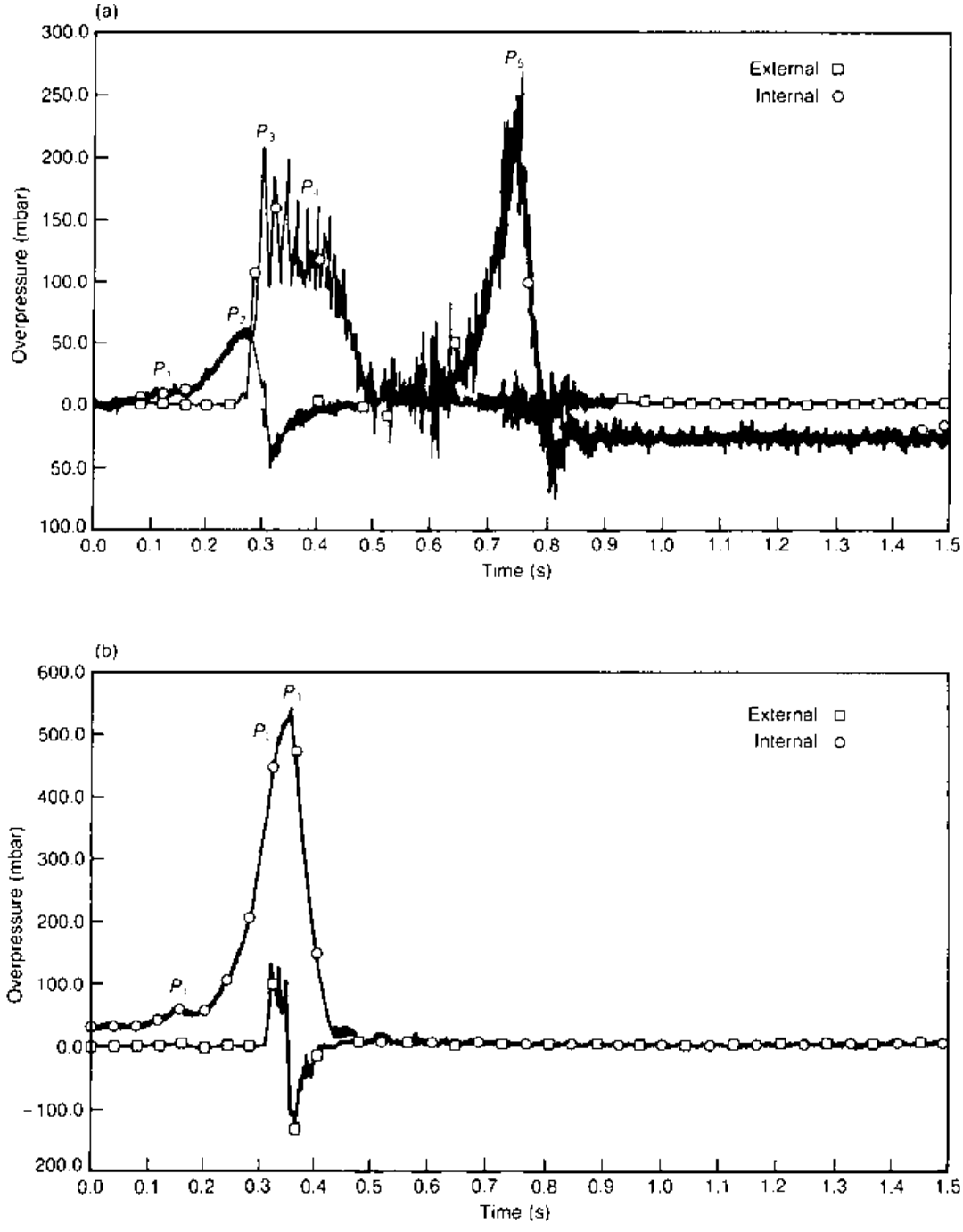


Figure 17.45 *Explosion venting of large enclosures: profiles of overpressure for explosions with different locations of the ignition source – 2 (Chamberlain, 1991; after A.J. Harrison and Eyre, 1987b) (Courtesy of the Institution of Chemical Engineers)*

oscillations and peak 5 due to acoustic coupling oscillations. The maximum peak pressure is at peak 5 at about 200 mbar. Figure 17.45(b) is for rear wall ignition. With ignition near the wall the oscillations are severely damped and peaks 2 or 3 dominate. In this particular case, the maximum peak pressure is at peak 3 at about 550 mbar.

17.15.3 Influencing factors

Some of the factors which influence the severity of a large vented explosion have been described by Chamberlain (1989). They include the fuel, the fuel/air ratio, the initial turbulence, the location of the ignition source, the size of the enclosure, the degree of obstruction and the vent area. The severity is increased if the fuel is a reactive one and if the fuel–air mixture is near stoichiometric. Initial turbulence will enhance the severity, but the effect is not readily quantifiable. The location of the ignition source has a strong effect. For a space with only one vent opening location of the ignition source furthest from the vent will tend to give the highest overpressures. The severity tends to increase with the volume of the enclosure and to decrease with the vent area.

Obstacles tend to have a very strong effect on the severity of the explosion. The effect depends on the number, dimensions and profile of the obstacles and on the resultant blockage ratio. Considering an obstructed region of grid arrays, the overpressure increases exponentially with the number of arrays. For obstacle dimensions a worst case diameter of between 50 and 250 mm has been observed in experiments. The effect of an obstacle having a sharp profile is about twice that of one with the same cross-section but with a rounded profile. The overpressure increases exponentially with blockage ratio. As far as the scale of the obstacles is concerned, large-scale obstacles have considerably smaller effect than corresponding configurations of small-scale obstacles.

The initial temperature has only slight influence as does the strength of the ignition source, leaving aside flame jet ignition.

17.15.4 External explosion

The occurrence of an external explosion has already been mentioned. The effect has been discussed by Chamberlain (1989).

The external explosion occurs because the advancing flame front expels unburned fuel from the vent. The external flow has a large and strong coherent structure and entrains a considerable quantity of air. When the flame emerges it constitutes a strong ignition source for this external flammable cloud and the external explosion can be severe. Its magnitude depends on the mass of fuel expelled, which in turn depends on the location of the ignition source. If all the fuel in the internal space is consumed before the flame reaches the vent, an external explosion will not occur. The external explosion will be weakened if the gas cloud is displaced far from the vent or if it is strongly diluted with air.

The influence of the external explosion on the internal overpressures is negligible where the latter exceeds 1 bar. At lower internal overpressures, however, the external explosion can have a marked effect. The larger the vent area and the lower the internal overpressure, the larger the relative contribution of the external explosion. Thus the external explosion is a factor which works against the attempt to limit the internal overpressures. There is some evidence that the importance of the external explosion increases with scale.

17.15.5 Computer codes

The computer codes available for the simulation of an explosion in a semi-confined enclosure were described in Section 17.9. These codes may be used, as there indicated, to investigate the course of an explosion with little or no venting, but their main application is to study situations in which there is appreciable venting.

There also exist codes designed specifically for venting calculations. One of these is the VENTEX code of Shell. This incorporates a semi-empirical model based on extensive experimentation. The code is used mainly for preliminary screening to investigate the effect of different parameters prior to use of more fundamental models. The VENTEX codes calculates first the overpressure in an empty enclosure at the instant when the flame reaches the vent, then the amplifying effect of obstacles and finally the effects of the external explosion.

17.15.6 Design methods

There is no full satisfactory fundamental method of predicting the overpressure from an explosion in a large vented enclosure. The available empirical equations are of limited use. They have usually been derived for empty vessels and tend not to take into account complicating factors such as internal obstacles or external explosions.

More useful are computer codes and model experiments. The former include the fundamental models incorporated in computer codes such as FLACS and CLICHE and the semi-empirical models of codes such as VENTEX. The use of the large CFD codes tends to be expensive.

Scale model experiments provide an alternative, or complement, to computer codes. This approach also is expensive.

Both computer codes and model experiments tend to involve a degree of extrapolation. It needs to be borne in mind that some phenomena become more significant as scale increases.

17.16 Venting of Reactors

The reactors which are considered here are liquid-phase reactors, essentially those capable of an exothermic reaction runaway.

It has long been the practice to protect such reactors against overpressure by the use of some form of relief such as a bursting disc or pressure relief valve. The overpressure protection of reactors was described in Chapter 11.

In this section an account is given of methods of sizing the vent for a reactor. Methods have progressed from early empirical correlations to methods based on various types of model, both simplified analytical models and full unsteady-state models embodied in computer codes.

One point is worth emphasizing at the outset. This is that in reactor venting it is the volumetric flow which is important.

The need for adequate vent sizing methods is evidenced by a number of incidents of reactor overpressure which have been attributed to the undersizing of the reactor vent.

Vent sizing of reactors is a complex and specialist matter. The account given here is no more than an overview.

17.16.1 Venting scenarios

The vent system for a reactor should be designed for the worst case scenario which is reasonably foreseeable. The scenarios considered should include fire engulfment as well as reaction runaway.

17.16.2 FIA method

An early method of vent sizing was the Factory Insurance Association (FIA) method, described by Sestak (1965). The method is an empirical one in which vent area is plotted as a function of reactor volume and reaction class. The graphical relations may be represented by the following approximate equation:

$$A = kV^{0.92} \qquad [17.16.1]$$

where A is the vent area (in.^{2}), V is the reactor capacity (US gal) and k is a constant. The constant k has the approximate values 0.0056, 0.021 and 0.095 ($V \leq 10\,000$) for exothermic reactions, categories A–D, with very low, low and moderately high heat releases, and 0.48 ($V \leq 4000$) for reactions with extraordinarily high heat releases. The value of k of 0.0056 is also used for endothermic reactions. The vent areas are given not as single lines but as bands of approximately ±50% about the values given by Equation 17.16.1.

The FIA method is relatively simple to apply and has been widely used. Examples of its use have been given by Harmon and Martin (1970).

A number of authors have discussed the method, including Duxbury (1976, 1980) and Fauske (1984a,b).

Fauske (1984b) has given the quantification of the FIA chart shown in Figure 17.46. This interpretation is based on the equation given by Fauske for the vent area of a vapour pressure system, given below as Equation 17.19.3, with properties of water ($\rho_l = 1000\,\text{kg/m}^3$, $C = 4.18\,\text{kJ/kg K}$ and $T = 373\,\text{K}$) and for an overpressure of 20%. The heat release rate q for the reaction categories A–D is quantified as shown in the figure.

Industrial Risk Insurers (IRI), the successor to FIA, withdrew the FIA method from its engineering procedures in the 1970s and recommended the use of other methods (Davenport, 1977c).

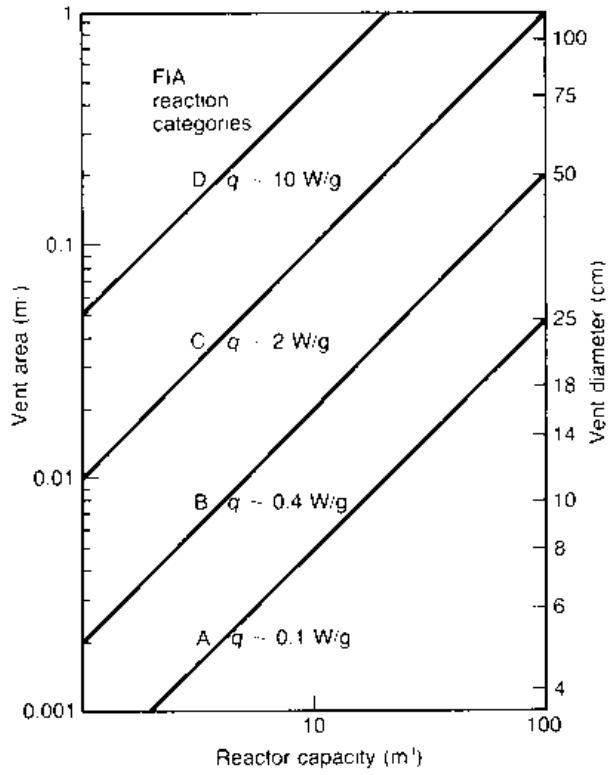


Figure 17.46 *Venting of chemical reactors: interpretation of FIA vent sizing method (Fauske, 1984b) q, energy release rate (Courtesy of the American Institute of Chemical Engineers)*

17.16.3 Monsanto correlation

Another simple method of vent sizing is the Monsanto correlation (W.B. Howard, 1973). This method is one of those included in a review given by Fauske (1984a). The correlation is used for sizing vents for runaway phenol–formaldehyde reactions. It is

$$D = 0.3V^{\frac{1}{2}} \qquad [17.16.2]$$

where D is the diameter of the vent (in.) and V is the volume of the reaction mass (US gal). The correlation is applicable for a self-heat rate of the order of 6.5°C/min and a set pressure of 15–16 psia. This implies a horizontal vent line to prevent build-up of static pressure due to liquid head.

17.16.4 Vent flow

The venting of a liquid-phase reactor is generally treated by determining (1) the flow of material which must be vented to prevent excessive overpressure and (2) the vent area required to effect this discharge.

The problem is complicated by the fact that it is difficult to predict whether the fluid discharged will be (1) a vapour, (2) a liquid or (3) a two-phase vapour–liquid mixture. Methods have been developed based on each of these assumptions. In general, the assumption of a single phase yields a simpler treatment, but the assumption of two-phase flow is more realistic.

It has often been observed that in practice the fluid vented from a reactor is not a vapour, but it either a liquid or a vapour–liquid mixture. Descriptions of incidents in which the charge was vented as either a liquid or a vapour–liquid mixture are given by Boyle (1967), Harmon and Martin (1970), Huff (1973, 1977a) and Duxbury (1976).

The general shape of the pressure curve for the venting of a runaway reaction as given by Harmon and Martin (1970) is shown in Figure 17.47. Figure 17.47(a) shows the curve for a runaway polymerization of ethyl acrylate with a vent of inadequate area and Figure 17.47(b) that for a runaway polymerization of methyl methacrylate with an adequate vent area.

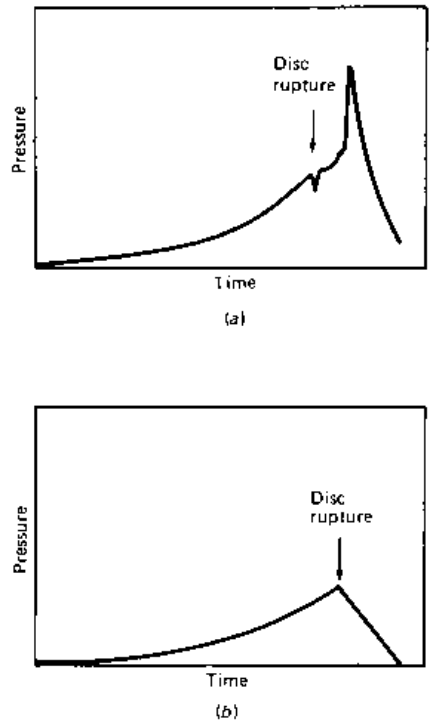


Figure 17.47 *Venting of chemical reactors: typical pressure curves for a runaway reaction (after Harmon and Martin, 1970): (a) vent area inadequate; (b) vent area adequate (Courtesy of the American Institute of Chemical Engineers)*

17.16.5 All vapour venting method

An approach to reactor venting which has frequently been adopted is that based on venting of the vapour from the boiling liquid reaction mass. This involves calculating the maximum allowable liquid temperature, which is related by the vapour pressure to the maximum allowable pressure, and then determining the rate of reaction and of heat generation at this temperature, the rate of vapour evolution and hence the flow of vapour to be generated.

The vent area is then

$$A = W/G \qquad [17.16.3]$$

with

$$W = \frac{r(-\Delta H_r)V}{\Delta H_v} \qquad [17.16.4]$$

where A is the vent area (m^2), G is the mass velocity ($kg/m^2 s$), ΔH_r is the heat of reaction (negative for exothermic reaction) (kJ/kg), ΔH_v is the latent heat of vaporization (kJ/kg), r is the rate of reaction ($kg/m^3 s$), V is the volume of the reaction mass (m^3) and W is the mass flow (kg/s).

The vent mass velocity G is determined by standard methods for vapour flow.

17.16.6 All liquid venting method

As mentioned above, however, it is known that in some cases the fluid is vented as a liquid or a vapour–liquid mixture.

An alternative approach, therefore, is to size the vent on the basis of discharging the whole reaction mass as a liquid. The required flow is calculated from the rate of reaction and of heat generation at the maximum liquid temperature and the time required to heat the reaction mass to this temperature.

Then

$$W = m_o/\Delta t \qquad [17.16.5]$$

with

$$\Delta t = \frac{m_o C\,\Delta T}{r(-\Delta H_r)V} \qquad [17.16.6]$$

where C is the specific heat of the reaction mass (kJ/kg K), m_o is the initial mass in the vessel, or the reaction mass (kg), Δt is the time interval to the maximum allowable pressure (s) and ΔT is the temperature

difference at equilibrium between the initial pressure and the maximum allowable pressure (K).

The vent area is again determined from Equation 17.16.3. The vent mass velocity G is determined by standard methods for liquid flow.

It is found that in some cases the all vapour venting method gives the larger area and in others the all liquid venting method.

17.16.7 Boyle method

A method based on the all liquid venting approach has been described by Boyle (1967). Effectively the method separates the calculation of the vent area from that of the vent flow. The latter is determined from the time for the reactor pressure to rise to the maximum allowable pressure. The former is estimated using the pressure in the reactor at the relief point.

The method given by Boyle is thus based on the pressure–time curve for the reactor. This may be obtained from the reaction rate or by experiment.

A statement of the Boyle model has been given by Leung (1986b) as follows:

$$W = \frac{m_o}{\Delta t_p} \qquad [17.16.7]$$

where Δt_p is the emptying time (s).

Leung also refers to the relation given by Fauske (1984b) for the emptying time

$$\Delta t_p = \frac{\Delta T}{(dT/dt)_s} \qquad [17.16.8]$$

where ΔT is the temperature rise corresponding to the overpressure ΔP (°C) and $(dT/dt)_s$ is the self-heat rate at the set pressure (°C/s).

Boyle recommends that the vent area be calculated by both the all vapour venting and the all liquid venting methods, that the larger area be used, and that a factor of safety of 2–3 be applied to the area so obtained.

A critique of Boyle's method is given by Duxbury (1980). In general, provided the flow is single phase the method tends to give vent sizes on the high side and thus to be conservative.

There is evidence from the work of Harmon and Martin (1970) that Boyle's method may underestimate the vent areas for larger reaction vessels. It gives for such vessels vent areas which are in some cases considerably less than those obtained by the FIA method. Further evidence is given Huff (1973, 1977a).

The method given by Boyle is not conservative for situations in which two-phase flow occurs. It is still possible, however, to use the first part of the method to calculate the flow to be vented, but to use two-phase flow methods for the vent sizing.

A modified Boyle method which takes account of two-phase flow has been described by Duxbury (1976). The two-phase flow calculations are performed using a fluid flow code.

17.16.8 Huff method

A method of vent sizing based on a much more comprehensive reactor model, including reaction kinetics and two-phase flow relations and embodied in a computer code, has been described by Huff (1973).

Huff also gives a comparison of the different methods of calculating vent sizes for liquid-phase reactors. For the case which he considers the two-phase flow model is more conservative that the FIA method or the all vapour venting and all liquid venting methods.

This model has undergone further development as described by Huff (1977a,b, 1982a,b, 1984a).

One version of this model (Huff 1977a,b, 1982a,b) has come to be known as the pseudo-steady state model (e.g. Duxbury and Wilday, 1989).

Duxbury (1980) describes this model as a two-phase venting method for reactions in which pressure and temperature peak simultaneously. Huff states that it is conservative for reactions in which pressure peaks first.

A statement of the Huff model has been given by Leung (1986b) as follows:

$$W = \frac{m_o}{\tau_t} - \frac{\beta}{2\tau_t^2}\left[\left(1 + \frac{4m_o\tau_t}{\beta}\right)^{\frac{1}{2}} - 1\right] \qquad [17.16.9]$$

with

$$\beta = \frac{h_{fg}V}{q_m v_{fg}} \qquad [17.16.10]$$

$$\tau_t = \Delta t_p + \frac{h_{fg}}{q_m}(x_m - x_o) \qquad [17.16.11]$$

$$x_m = \frac{V/m_m - v_f}{v_{fg}} \qquad [17.16.12]$$

$$m_m = m_o - W\tau_t \qquad [17.16.13]$$

where h_{fg} is the latent heat of vaporization (kJ/kg), m is the reaction mass in the vessel (kg), q is the heat release rate per unit mass (kW/kg), x is the mass fraction of vapour, or quality, v_f is the specific volume of the liquid (m^3/kg), v_{fg} is the specific volume change between the vapour and liquid phases (m^3/kg), β is a parameter, τ_t is the turnaround time for temperature (s), and the subscripts m and o denote at peak pressure (or temperature) and initial, respectively.

17.16.9 BPF method

Another full unsteady-state model is that developed for phenolic resin reactors by the British Plastics Federation (BPF) and described by Booth *et al.* (1980).

17.16.10 Scale-up methods

An alternative approach to the vent sizing of liquid phase reactors is scale-up from experimental tests. Such extrapolation is valid, however, only if similarity exists between the test and full-scale systems.

Some of the conditions which must be met before similarity can be assumed are listed by Duxbury (1976). Thus for polymerization reactions he suggests that the basis for scaling up, though not for scaling down, might be a constant ratio of vent area to reactor volume. This accords quite well with the FIA method in which vent area increases with reactor volume to the power 0.92.

17.16.11 ICI methods

Reviews of methods of vent sizing used in ICI have been given by Duxbury (1976, 1980) and by Duxbury and Wilday (1987, 1989, 1990). An account of the ICI scheme is given in Section 17.21.

17.16.12 Reaction parameters

As already indicated, there are a number of reactor parameters which are relevant to reactor venting. They include:

P_s Set pressure

$(dT/dt)_s$ Self-heat rate, at set pressure

Q_g Gas evolution rate

Q_v Vapour evolution rate

where P_s is the set pressure (Pa), Q_g is the volumetric gas evolution rate (m^3/s), Q_v is the volumetric vapour evolution rate (m^3/s) and $(dT/dt)_s$ is the self-heat rate (°C/s).

17.16.13 Source term

The flow entering the vent may be a homogeneous vapour–liquid equilibrium mixture or, if vapour disengagement occurs, a vapour. The size of vent required is different for the two cases.

When the reactor pressure is reduced due to venting, the liquid becomes superheated and vapour bubbles are formed, causing liquid swell. Unless vapour disengagement occurs, a two-phase mixture will enter the vent. Vapour disengagement does tend to occur in non-foamy system, though not in foamy ones.

Definition of the source term for the flow entering the vent is therefore of some importance. This is considered in Chapter 15.

17.16.14 Relief devices

The relief devices normally used for venting of liquid-phase reactors are bursting discs or pressure relief valves.

It is necessary to allow for two-phase flow through these devices. This is dealt with in Chapter 15.

17.16.15 Relief disposal

The material vented must be disposed of safely. Relief disposal is considered in Sections 17.22 and 17.23.

17.16.16 Containment

In certain cases, as discussed by Duxbury (1976), containment of a possible runaway reaction may be an attractive alternative to venting. This may be so, for example, if the peak pressure attainable is close to the working pressure or if it is less than the minimum design pressure for a vessel of that size or if there are special venting problems such as blockage of the vent lines.

The application of this concept to reactors has been developed by Wilday (1991). An account is given in Chapter 12.

17.16.17 Instrumented systems

Another design option for reactor venting is the use of an instrumentation and control system designed to ensure that overpressure does not occur and thus to eliminate the need for venting. This approach is discussed in Chapters 11, 12 and 13.

17.16.18 Design conservatism

It is generally desirable in design to adopt a conservative approach, but in reactor venting, care is needed in defining what this means. A low mass velocity through the vent is conservative with regard to determination of the vent area. But it is not conservative with respect to pressure drops in the system, reaction forces caused by the venting or load on the relief system.

17.16.19 DIERS

It was recognized towards the end of the 1970s that understanding of reactor relief was deficient and that methods of vent sizing were inadequate and a major international co-operative project, DIERS, was initiated to remedy this. This project is now described.

17.17 Venting of Reactors and Vessels: DIERS

17.17.1 DIERS project

A major project on reactor venting was undertaken during the mid-1980s by the Design Institute for Emergency Relief Systems (DIERS) of the American Institute of Chemical Engineers (AIChE) with sponsorship from a large international group of companies. The main contractor was Fauske and Associates Inc., and results from the project and its aftermath have been the subject of a series of publications by Fauske and co-workers, notably Epstein, Grolmes, Leung and Swift. Overviews of the project have been given by H.G. Fisher (1985, 1991).

The work is described in the *DIERS Project Manual*, which gives a overview and contains chapters on the following aspects: vapour disengagement; relief system flow; large scale tests; high viscosity flashing flow; mechanical design, containment and disposal; bench-scale apparatus; and the SAFIRE computer code.

Some principal elements of the work are given in the *Technology Summary*. This deals with the behaviour of the vapour in the vessel and with vapour–liquid flow in the vent line and gives emergency relief system (ERS) design methods. It also deals with fire relief of storage vessels.

The DIERS project involved an extensive investigation of the behaviour of the fluid venting through the vent line. It included study of the vapour disengagement in the vessel and of the fluid flow through the vent. The work showed that there are different types of reaction system and that the behaviour of these systems is different. A major finding was that the flow at the vent tends to be a two-phase vapour–liquid flow. Methods of ERS design were developed for the different systems. These included simplified methods, a computer model and a scale-up method. A bench-scale apparatus was designed capable of determining the principal design parameters.

There is a DIERS Users Group which is described by H.G. Fisher (1989). A newsletter of the group has been carried in *Plant/Operations Progress*.

17.17.2 Influencing factors

The overall venting behaviour of reaction system depends on a number of factors. They include (1) reaction regime, (2) vapour disengagement, (3) fluid viscosity and (4) vent line length. It is necessary to allow

for these factors in design, and in particular to take them into account in scale-up from bench scale to full scale.

17.17.3 Reaction regimes

The different types of reaction system, or reaction regimes, distinguished in the work are

(1) vapour-generating system;
(2) gas-generating system;
(3) hybrid system.

A vapour-generating system is one in which the total pressure is the system vapour pressure. In other words, the system contains one or more high vapour pressure components. When the vent opens, tempering of the reaction occurs due to the cooling associated with the latent heat of vaporization. Such a system is also referred to as a high vapour pressure, or vapour pressure, system or a tempered system.

In a gas-generating system, by contrast, there is no high vapour pressure component, and the total pressure is that of the gaseous components. The reaction is not tempered and its course is essentially independent of the venting process. Such a system is also referred to as a gassy system or a non-tempered system.

The intermediate case is that of a hybrid system, and its behaviour is intermediate between that of a pure vapour pressure system and a pure gassy system. A degree of tempering occurs.

17.17.4 Vessel behaviour

The nature of the fluid which enters the vent depends on the flow regime in the vessel when the vent opens, and the vessel is depressurized. There are two flow regimes, the bubbly, or foaming, regime and the churn turbulent regime. In the former there is little vapour disengagement and the vapour–liquid mixture entering the vent line is essentially the same as that in the vessel itself. In the latter regime there is significant vapour disengagement.

Methods exist which allow an estimate to be made for vapour disengagement in systems with pure substances, but not in reacting systems.

In practice, therefore, for venting of a reaction mass it is generally necessary to fall back on the default assumption that there is no vapour disengagement and that the fluid entering the vent is a homogeneous two-phase vapour–liquid mixture.

A considerable amount of work was done, however, to increase understanding of liquid swell and vapour disengagement. An account of these aspects is given in Chapter 15.

17.17.5 Bench-scale equipment: apparatus

As already indicated, it is sometimes preferable to base the vent design on experimental tests. There are, however, certain pitfalls in scale-up from bench to full scale. A suitable design of test apparatus provides a safeguard against these. The design of such apparatus was another task undertaken in the DIERS project.

A low heat capacity test cell was designed with a capacity of 120 ml and a ϕ factor of about 1.05. This equipment is generally referred to as the bench scale apparatus and is also known as the Vent Sizing Package (VSP). This apparatus is shown in Figure 17.48. It has

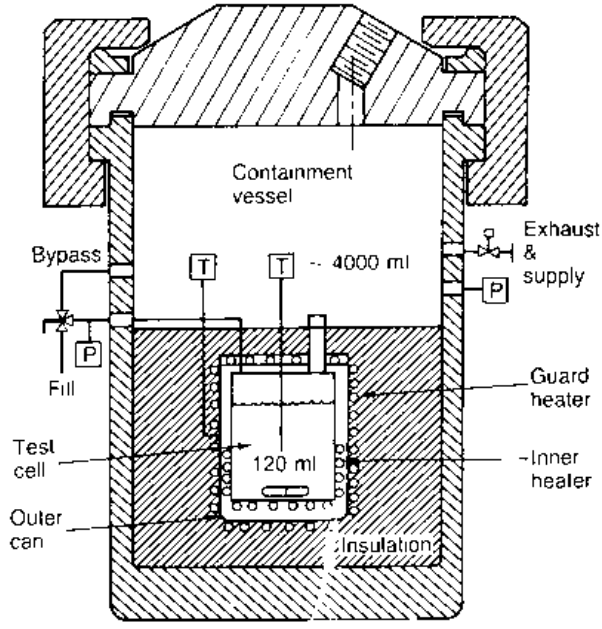


Figure 17.48 *Venting of chemical reactors: Vent Sizing Package (Fauske and Leung, 1985) (Courtesy of the American Institute of Chemical Engineers)*

been described by Fauske and Leung (1985) and Fauske (1988a).

As stated in Chapter 11, the ϕ factor is the ratio of the heat capacity of the sample plus cell to that of the sample alone, and a value close to unity means that the temperature rise measured is close to the actual temperature rise of the sample.

Another apparatus, distinct from the VSP and developed later, is the Reactive System Screening Tool (RSST), described by Creed and Fauske (1990). The RSST is a test cell with a capacity of about 10 ml and a ϕ factor of about 1.04. The authors state that the ease of use approaches that of DSC and the accuracy that of the VSP. The RSST may be used for the measurement of the rate of temperature rise, and hence the energy release rate in a vapour pressure system, or to determine the rate of pressure rise, and hence the gas evolution rate in a gassy system. It may also be used for direct scale-up.

17.17.6 Bench-scale equipment: application

For a vapour pressure system, it is necessary for vent sizing to know the rate of temperature rise, or self-heat rate, and hence the energy release rate. This may be measured using the VSP.

In addition, if the reaction mixture is highly viscous and the vent flow likely to be laminar, the apparatus may be used to determine the vent flow.

For a gassy system, the information required is the rate of pressure rise and hence the peak gas evolution rate. The VSP may be used to measure this. It may also be used to obtain the vent flow, though generally gassy systems are not particularly viscous.

These reaction parameters are then used in the appropriate vent sizing relationships.

Alternatively, the VSP may also be used to carry out direct scale-up.

The application of the bench scale equipment, and the relationships with which it is used, are described further in Section 17.19.

17.17.7 Vent flow models

A number of models for vent flow were developed by DIERS. These are given in the *Technology Summary* and have been described in papers by Fauske and co-workers. An account of these models is given in Section 17.18.

17.17.8 Vent area

DIERS developed methods for the sizing of vents for vapour pressure, gassy and hybrid systems. These are outlined in the *Technology Summary* and described by Fauske and co-workers. Section 17.19 gives an account of these methods.

In some cases it may be possible to use vent sizing correlations without resort to experimentation, but in other cases experimental work is essential.

17.17.9 Scale-up

The bench scale equipment may be used to determine the vent area by vent area/reaction mass scaling using direct scaling relationships. This approach is to be distinguished from the use of the apparatus to determine parameters such as self heat rate or gas evolution rate which are then utilized in vent sizing equations which require these parameters.

17.17.10 Numerical model

The DIERS project also involved the development of a numerical model of the venting of a reactor based on a full set of differential equations for the reaction kinetics and thermal and fluid flow effects. The model is essentially an unsteady-state heat balance with supporting equations. This model is referred to as the integral model and is the basis of the computer code SAFIRE described below. An account of the model has been given by Grolmes and Leung (1985).

17.17.11 SAFIRE code

The integral model is the core feature of the computer program SAFIRE (System Analysis for Integrated Relief Evaluation) developed as part of the project. This has been described by Grolmes and Leung (1985).

The program requires as input, data on the physical and thermodynamic properties of the mixture, the reaction stoichiometry and kinetics, the vessel and vent line geometry and selection of the flow model assumptions.

The vessel geometries handled are a vertical cylinder, a horizontal cylinder and a sphere. The vent entry location can be at the top or bottom of the vessel. The vent may be an effectively frictionless nozzle, a nozzle fitted with a safety relief valve, or a vent line in which friction is significant. The latter may have a single segment, two segments with a change of cross-section, or three segments with a safety relief valve followed by a change in cross-section.

Vessel flow regimes incorporated are all vapour, all liquid, homogeneous mixture and partial disengagement regimes. Vent line flow models are as follows. There are both all vapour flow and all liquid flow models. Nozzles models include the ERM, the homogeneous equilibrium flashing model and the frozen homogeneous model. For long vent lines the models are the homogeneous equilibrium model and the slip equilibrium model.

The program may be run in three modes: pre-relief, post-relief or combined.

The authors describe the use of the code to simulate a number of experimental tests on styrene and on ethylbenzene.

17.17.12 Experimental tests

The DIERS programme included a series of experimental tests, both at laboratory scale and on a larger scale. An account of the larger scale tests in Phase III of the project has been given by Grolmes, Leung and Fauske (1985).

The test vessels used were a 32 litre vessel and a 2200 litre vessel. The latter had a 12 000 litre catchtank.

A set of 70 tests were performed, including 25 with the larger vessel. Water was used in 15 tests with the smaller vessel and 20 tests with the larger one. Using ethylbenzene, four tests were performed in the smaller vessel and none in the larger, whilst using styrene 16 tests were done in the smaller vessel and five in the larger.

The configurations studied included both top and bottom vent locations and both nozzles and long vent lines.

The systems tested were all vapour pressure systems. The principal feature investigated in the tests was vapour disengagement. The work showed that vapour

disengagement and the associated churn turbulent regime were confined to non-foaming and non-viscous systems.

17.17.13 Non-Arrhenius behaviour

The low heat capacity test cell was used to investigate a number of systems. One of the effects observed is noteworthy.

As described by Fauske (1985a), tests were performed on a 50/50 mixture of zinc peroxide/zinc oxide at two different heating rates. The test at the lower heating rate obeyed the classic Arrhenius relation between temperature and reaction rate as evidenced by the pressure rise, that at the higher heating rate did not, but gave a much sharper pressure rise, presumably due to a hot spot.

17.18 Venting of Reactors and Vessels: Vent Flow

A general account of two-phase flow models was given in Chapter 15. The account given here is confined to those models used for the venting of reactors and storage vessels.

There are a number of relations used in the DIERS work for the mass flux of fluid flowing out of the vent and down the vent line. Accounts are given by Fauske (1984b,c, 1985a), Grolmes and Leung (1985) and Leung (1986b) and in the *Technology Summary*.

Leung (1986b) has reviewed flow models for venting of a vapour pressure, or tempered, system. He considers frictionless flow and a short vent line ($L/D < 50$). The models include:

(1) the non-flashing liquid flow;
(2) the homogeneous equilibrium model;
(3) the equilibrium rate model;
(4) the homogeneous non-equilibrium model;
(5) the slip equilibrium model.

For a simple orifice in the side of a vessel the outflow may be determined by treating the fluid as a non-flashing liquid.

For other cases the homogeneous equilibrium model (HEM) is generally the most appropriate. It gives lower flows over the entire two-phase region and is to this extent conservative for ERS design. However, it is realistic rather than overly conservative and agrees well with experimental data. The original HEM model is somewhat complex and requires extensive thermodynamic data, but a more convenient version requiring only stagnation properties has been developed by Leung (1986a).

An alternative model is the equilibrium rate model (ERM) of Fauske (1985b), who has developed the model to deal with a number of different situations.

For the all-liquid inlet condition, Leung has given a version of his approximate HEM model which is similar in form to the ERM model, as described below.

The equilibrium condition is closely approached for pipes longer than 0.1 m. Where the vent line is shorter than this, the homogeneous non-equilibrium model of R.E. Henry and Fauske (1971), the HFM model, may be used to estimate the flow.

Leung also discusses the use of the slip equilibrium model (SEM) of F.J. Moody (1965).

Some of the principal flow models are now described. An account of those used in the DIERS work is given in the *Technology Summary*.

17.18.1 Vapour pressure systems

A family of flow models for venting of vapour pressure systems has been described by Fauske (1984a,b, 1985a,b) in the context of DIERS, in particular the ERM.

The base case is choked non-equilibrium flashing frictionless flow. For this case Fauske gives

$$G \approx \frac{h_{fg}}{v_{fg}} \left(\frac{1}{NTC} \right)^{\frac{1}{2}} \qquad [17.18.1]$$

with

$$N \approx \frac{h_{fg}^2}{2\ \Delta P\ \rho_l K^2 v_{fg}^2 TC} + 10L \qquad [17.18.2]$$

where K is the discharge coefficient, L is the length of the vent pipe (m), ΔP is the total available pressure drop (Pa), T is the absolute temperature (K), ρ_l is the density of the liquid (kg/m^3) and N is a non-equilibrium parameter. For a sharp-edged orifice K is 0.61.

For no vent line ($L = 0$) Equation 17.18.1 reduces to

$$G = K(2\ \Delta P\ \rho_l)^{\frac{1}{2}} \qquad [17.18.3]$$

For a vent line long enough for equilibrium conditions to apply ($L \geq 0.1$ m) the parameter N is unity, and Equation 17.18.1 becomes

$$G = \frac{h_{fg}}{v_{fg}} \left(\frac{1}{TC} \right)^{\frac{1}{2}} \qquad [17.18.4]$$

There is an alternative formulation of Equation 17.18.4 based on the relation between vapour pressure P and temperature T:

$$G = \frac{\mathrm{dP}}{\mathrm{d}T} \left(\frac{T}{C} \right)^{\frac{1}{2}} \qquad [17.18.5]$$

Equation 17.18.5 implies

$$\left(\frac{\mathrm{dP}}{\mathrm{d}T} \right)^2 \frac{T}{C} = \left(\frac{h_{fg}}{v_{fg}} \right)^2 \frac{1}{TC} \qquad [17.18.6]$$

Equations 17.18.4 and 17.18.5 are the ERM. For venting the rate of change of pressure with temperature is $\Delta P/\Delta T$. In Fauske's work for this model the mass flux is frequently written as G_{ERM} so that

$$G_{ERM} = \frac{\Delta P}{\Delta T} \left(\frac{T}{C} \right)^{\frac{1}{2}} \qquad [17.18.7]$$

where ΔP is the overpressure (Pa) and ΔT is the temperature rise corresponding to overpressure ΔP (°C).

Further, it is assumed in the model that the flow is turbulent. Where this aspect is emphasized the mass velocity is written as G_T so that

$$G_T = \frac{\Delta P}{\Delta T} \left(\frac{T}{C} \right)^{\frac{1}{2}} \qquad [17.18.8]$$

Equation 17.18.8 is used where there is homogeneous equilibrium flow, there is a moderate overpressure (≈20%) and the flow is turbulent.

Normally the vent line will be long enough for equilibrium flow to be assured. For the case where

there is a very short vent line ($0 < L < 0.1$ m), the mass flow may be obtained by interpolation between Equations 17.18.3 and 17.18.8.

For a long vent line Fauske (1989a) introduces into Equation 17.18.8 a correction factor F to give

$$G_T = F\frac{\Delta P}{\Delta T}\left(\frac{T}{C}\right)^{\frac{1}{2}} \quad [17.18.9]$$

with

$$F = f(L/D) \quad [17.18.10]$$

where D is the diameter of the vent line (m) and F is a correction factor for vent line length.

The flow correction factor F is a function of the length/diameter ratio L/D. Slightly different correlations have been given in different papers. That currently used for vapour pressure systems is that given by Fauske, Grolmes and Clare (1989), and is:

L/D	F
0	1.0
50	0.8
100	0.7
200	0.6
300	0.55
400	0.5

The original values of F were 0.85, 0.75, 0.65 and 0.55 at L/D ratios of 50, 100, 200 and 400, respectively (Fauske, 1989a).

If the flow is highly viscous, it may be laminar. The relation given by Fauske (1987b, 1989a) for the mass velocity G_L for this case is

$$G_L \approx \left(\frac{h_{fg}}{v_{fg}}\right)^2 \frac{1}{TC}\frac{1}{32\mu}D\frac{D}{L} \quad [17.18.11]$$

$$= \left(\frac{dP}{dT}\right)^2 \frac{T}{C}\frac{1}{32\mu}D\frac{D}{L} \quad [17.18.12]$$

where D is the diameter of the vent line (m) and μ is the viscosity (kg/m s).

In practice the liquid viscosity for the reaction mixture is generally not known. In this case, therefore, the bench scale apparatus may be used to determine the mass flow. Relations for this case are given by Fauske (1989a) in terms of the required vent diameter and are therefore described in Section 17.19.

17.18.2 Gassy systems

For gassy systems one DIERS approach is to utilize the bench scale apparatus to determine the flow.

Leung and Fauske (1987) have used for such systems the method of Tangren, Dodge and Seifert (1949). Leung (1992b) has also given a method of his own.

Fauske (1985a) gives as a reasonable upper bound for the mass velocity the relation

$$G = [2(P_s - P_a)\rho_l(1-\alpha)]^{\frac{1}{2}} \quad [17.18.13]$$

where P_a is the atmospheric pressure (Pa), P_s is the set pressure (Pa) and α is the initial vapour fraction. Equation 17.18.13 is suitable for use where some overestimation of flow may be acceptable such as in sizing of the relief equipment.

17.18.3 Hybrid systems

For hybrid systems there is again no entirely satisfactory flow relation, and one DIERS approach is to utilize the bench scale apparatus to determine the flow.

For a hybrid system Fauske (1985b) gives the following approximate relations:

$$G \approx (2P_g\rho_l + G_{ERM}^2)^{\frac{1}{2}} \quad [17.18.14]$$

with

$$G_{ERM} \approx \frac{P_v}{P}\frac{dP}{dT}\left(\frac{T}{C}\right)^{\frac{1}{2}} \quad [17.18.15]$$

$$P = P_v + P_g \quad [17.18.16]$$

where P_g is the partial pressure of the gas (Pa) and P_v is the partial pressure of the vapour (Pa).

17.18.4 Storage vessels

For flow of a flashing liquid from the liquid space of a storage vessel, Fauske (1985b) distinguishes between a saturated liquid and a subcooled liquid. For a saturated liquid he gives

$$G = 0.6[2(P_o - P_a)\rho_l]^{\frac{1}{2}} \qquad L = 0 \quad [17.18.17]$$

$$G_{ERM} = \frac{\Delta P}{\Delta T}\left(\frac{T}{C}\right)^{\frac{1}{2}} \qquad L > 0.1\text{ m} \quad [17.18.18]$$

where P_o is the absolute stagnation pressure (Pa).

For a subcooled liquid Fauske gives

$$G = 0.6[2(P_o - P_a)\rho_l]^{\frac{1}{2}} \qquad L = 0 \quad [17.18.19]$$

$$G = [2(P_o - P(T_o))\rho_l + G_{ERM}^2]^{\frac{1}{2}} \qquad L > 0.1\text{ m} \quad [17.18.20]$$

where T_o is the absolute stagnation temperature (K).

17.18.5 Vapour pressure systems: homogeneous equilibrium model

The family of flow relations given above is that of Fauske and the principal model is the ERM. An alternative model for equilibrium flow is the HEM.

This model has been formulated in convenient form by Leung (1986b), who gives the following relations. For the high and low quality regions, respectively, the equations are

$$\frac{G}{(P/v)^{\frac{1}{2}}} = \frac{0.66}{\omega^{0.39}} \qquad \omega < 4.0 \quad [17.18.21a]$$

$$\frac{G}{(P/v)^{\frac{1}{2}}} = \frac{0.6055 + 0.1356\ln\omega - 0.0131(\ln\omega)^2}{\omega^{0.5}} \qquad \omega \geq 4.0 \quad [17.18.21b]$$

with

$$\omega = \frac{xv_{fg}}{v} + \frac{CTP}{v}\left(\frac{v_{fg}}{h_{fg}}\right)^2 \qquad [17.18.22]$$

$$v = v_f + xv_{fg} \qquad [17.18.23]$$

where P is the pressure (Pa), v is the specific volume of the mixture (m^3/kg) and ω is the critical flow scaling parameter.

For an all liquid inlet flow, Equation 17.18.21 may be approximated by

$$G \approx 0.9\frac{h_{fg}}{v_{fg}}\left(\frac{1}{TC}\right)^{\frac{1}{2}} \qquad [17.18.24]$$

This equation is similar in form to Equation 17.18.4 except for the factor 0.9. The flow given by it is termed by Grolmes and Leung (1984) the limiting flow.

Leung (1986b) has given a set of models for vent sizing for vapour pressure systems, which is described in Section 17.20. These models are independent of the expression used for the mass velocity G, but the flow model quoted in that account is the HEM as just outlined.

17.19 Venting of Reactors and Vessels: Vent Sizing

Some of the methods available for vent sizing prior to the DIERS project were described in Section 17.16. An account is now given of methods developed in DIERS.

The bench scale apparatus used in some of the methods is described in Section 17.17.

17.19.1 Vapour pressure systems

For a vapour pressure system, it is necessary to know the self-heat rate. One option for obtaining this is the use of the bench scale apparatus. But it may be possible to determine it without resort to experiment.

Given the self-heat rate, the following simplified method has been described by Fauske (1984b) for the vent area:

$$A = \frac{V\rho}{G\,\Delta t_v} \qquad [17.19.1]$$

with

$$\Delta t_v = \frac{\Delta T\,C}{q_s} \qquad [17.19.2]$$

where q_s is the energy release rate at the set pressure (kW/kg), Δt_v is the venting time (s) and ρ is the density of the reaction mass (kg/m^3).

Combining Equations 17.19.1 and 17.19.2 with Equation 17.18.7 gives

$$A = V\rho(TC)^{-\frac{1}{2}}\frac{q_s}{\Delta P} \qquad [17.19.3]$$

Equations 17.18.7 and 17.19.3 are based on the assumption that the flow in the vent line is homogeneous equilibrium flow and that it is turbulent and are intended for use where there is a modest overpressure in the range 10–30%, say 20%.

For a frictionless vent line, Equation 17.19.3 predicts a vent area larger by a factor of less than 2 than that given by the integral model, assuming homogeneous vessel behaviour and homogeneous equilibrium flow.

The mass flow is relatively insensitive to the length diameter ratio L/D. It varies by less than a factor of 2 for L/D up to 400. Most vent lines are 5–10 m in length.

17.19.2 Vapour pressure systems: Fauske nomograph

For a vapour pressure system, a generalized vent sizing nomograph based on Equation 17.19.3 was published in 1984 by Fauske (1984a). A revised nomograph, given below, was published in 1988.

This initial nomograph was based on the assumptions of turbulent flow and a modest overpressure.

Fauske (1984a) has compared the nomograph method with some of the earlier methods of vent sizing described above. He considers three different duties, one for the Monsanto method, one for the BPF and Huff methods, and one for the SAFIRE method. His results may be summarized as follows:

	Vent area (m^2) *from:*	
Method	*Method named*	*Nomograph*
Monsanto	Area = 0.0125 m^2/1000 kg	Area = 0.012 m^2/1000 kg
BPF	Area = 0.026 m^2/1000 kg	Area = 0.0145 m^2/1000 kg
Huff code	Diameter = 33.7 cm	Diameter 34 cm
SAFIRE code	Diameter = 15.8 cm ($L/D \approx 100$) = 18 cm ($L/D \approx 400$)	Diameter ≈ 18.5 cm

17.19.3 Vapour pressure systems: high viscosity systems

For a high viscosity system, the flow in the vent line is likely to be laminar. The bench scale apparatus may be used to determine an actual flow. Then, as described by Fauske (1989), the diameter of the full scale vent line may be obtained from the relations

$$D_L = D_T \qquad G_o(D_T/D_o) \geq G_T \qquad [17.19.4a]$$

$$\approx \left(D_T^2 D_o \frac{G_T}{G_o}\right)^{\frac{1}{3}} \qquad G_o(D_T/D_o) < G_T \qquad [17.19.4b]$$

where D_L is the diameter of the full scale vent line for laminar flow (m), D_o is the diameter of the vent line in the bench scale apparatus (m), D_T is the diameter of the full-scale vent line for turbulent flow (m), G_o is the mass velocity in the bench scale apparatus ($kg/m^2\,s$), G_T is the mass velocity at full scale in turbulent flow ($kg/m^2\,s$).

According to the *Technology Summary*, viscous effects on level swell are generally not important if the liquid viscosity is below 100 kPa s.

17.19.4 Vapour pressure systems: revised Fauske nomograph

A revised method for vapour pressure systems, and an associated nomograph, have been given by Fauske, Grolmes and Clare (1989). The relation given for the vent area is

$$A = \frac{5}{2}\frac{Q_v}{F(TC)^{\frac{1}{2}}P_s}\frac{\alpha_d - \alpha_o}{1 - \alpha_o} \qquad [17.19.5]$$

Table 17.19 *Venting of chemical reactors: flow reduction factor* ***F*** *in Fauske vent sizing correlations (Fauske, Grolmes and Clare, 1989) (Courtesy of the American Institute of Chemical Engineers)*

L/D	*All vapour flow* I	*Vapour pressure system, two-phase flashing flow* II	*Gassy system, two-phase non-flashing flow* III
0	1.0	1.0	1.0
50	0.8	0.8	0.71
100	0.7	0.7	0.58
150	0.65	0.65	0.50
200	0.60	0.60	0.45
250	0.58	0.58	0.41
300	0.55	0.55	0.38
350	0.52	0.52	0.35
400	0.50	0.50	0.33

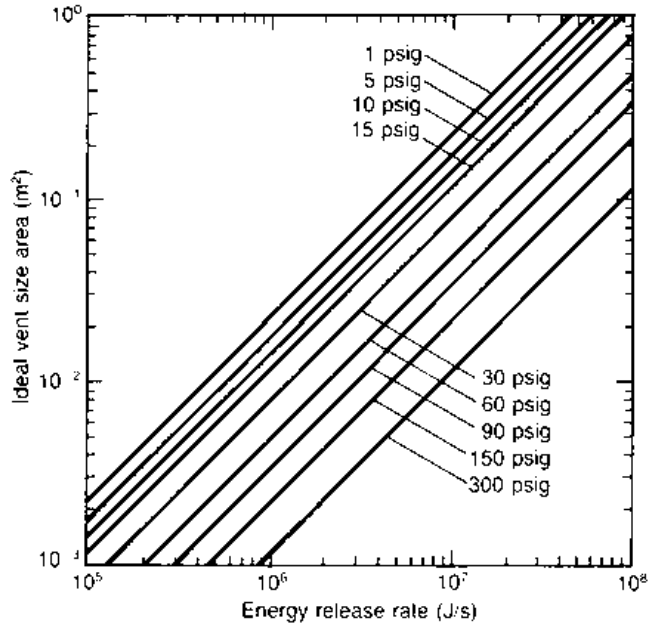


Figure 17.49 *Venting of chemical reactors: nomograph for vent sizing for a vapour pressure system (Fauske, Grolmes and Clare, 1989) (Courtesy of the American Institute of Chemical Engineers)*

where α is the void fraction and the subscripts d and o denote the disengagement and initial, or freeboard, value, respectively.

The flow reduction factor F for use in Equation 17.19.5 is given in Table 17.19, column II.

Figure 17.49 is a nomograph based on Equation 17.19.5. The nomograph is for the following conditions: $C = 2500\,\mathrm{J/kg\,K}$, $T = 400\,\mathrm{K}$, $\alpha_\mathrm{d} = 1$ and $L/D = 0$. It is therefore applicable to the case of no vapour disengagement.

17.19.5 Vapour pressure systems: extended method for vapour disengagement

As described by Grolmes, Leung and Fauske (1983), interpretation of the DIERS data has shown that during two-phase venting relatively large deviations in the equilibrium between the vapour and the liquid may exist.

The implications are discussed by Fauske (1989a). It is virtually impossible to predict the vapour/liquid ratio entering the vent line. The absence of equilibrium means that following actuation of the relief the temperature continues to rise, but without a corresponding overpressure. In due course a 'turnaround', or 'turnover', of temperature occurs.

Fauske states that in most practical systems there is likely to be only modest superheating (10–20°C) and that temperature turnaround should be assured before the onset of vapour disengagement. The rate of loss of reaction mass can be assumed to be largely independent of the vapour/liquid ratio of the mixture entering the vent line.

On these assumptions, an extension of the method was developed which takes into account vapour disengagement, as described by Fauske (1987a,b). The extension requires information on the self-heat rate. The relation given for the vent area, assuming turbulent flow, is

$$A = \frac{1}{2}\frac{m_o(dT/dt)_s(\alpha_d - \alpha_o)}{F(T/C)^{\frac{1}{2}}\Delta P(1-\alpha_o)} \qquad 0.1 \le \frac{\Delta P}{P_s} \le 0.3 \quad [17.19.6]$$

where ΔP is the overpressure (Pa).

The loss of reaction mass at time of turnaround, given by Fauske (1988a, 1989a), is

$$G \approx \frac{1}{A\,\Delta t_v} m_o \frac{\alpha_d - \alpha_o}{1-\alpha_o} \quad [17.19.7]$$

where Δt_v is the time to temperature turnaround (s), given by

$$\Delta t_v \approx \frac{2\,\Delta T}{(dT/dt)_s} \quad [17.19.8]$$

17.19.6 Gassy systems

For gassy systems, it is necessary to know the peak gas generation rate. It is usually necessary to use the bench scale apparatus to obtain this.

Then as given in the *Technology Summary* (Equation 2.4) the vent area is

$$A = \frac{Q_g(1-\alpha)\rho_l}{G} \quad [17.19.9]$$

$$= \frac{Q_g m}{GV} \quad [17.19.10]$$

where m is the mass of mixture in the vessel (kg) and Q_g is the peak volumetric gas evolution rate (m^3/s).

17.19.7 Gassy systems: Fauske nomograph

A method for gassy systems, and an associated nomograph, have been given by Fauske, Grolmes and Clare (1989). The relation given for the vent area is

$$A = \left(\frac{1}{2}\right)^{\frac{1}{2}} \frac{Q_g}{F}\left(\frac{\rho_l}{P - P_a}\right)^{\frac{1}{2}} \quad [17.19.11]$$

where P is the absolute pressure (Pa) and P_a is the absolute atmospheric pressure (Pa). (In the authors' paper the term $P - P_a$ is written as P where the latter is a gauge pressure).

The flow reduction factor F for use in Equation 17.19.11 is given in Table 17.19, column III.

Figure 17.50 is a nomograph based on Equation 17.19.11. The nomograph is for the following conditions: $\rho_l = 1000\,kg/m^3$ and $L/D = 0$.

17.19.8 Hybrid systems

For hybrid systems, the situation is more complex. The behaviour of the system depends on whether it is tempered or non-tempered.

Untempered hybrid systems have generally to be treated as gassy systems.

A relation for the vent area at initiation of homogeneous two-phase venting, reflecting the worst case, is given in the *Technology Summary* (Equation 2.5) as follows:

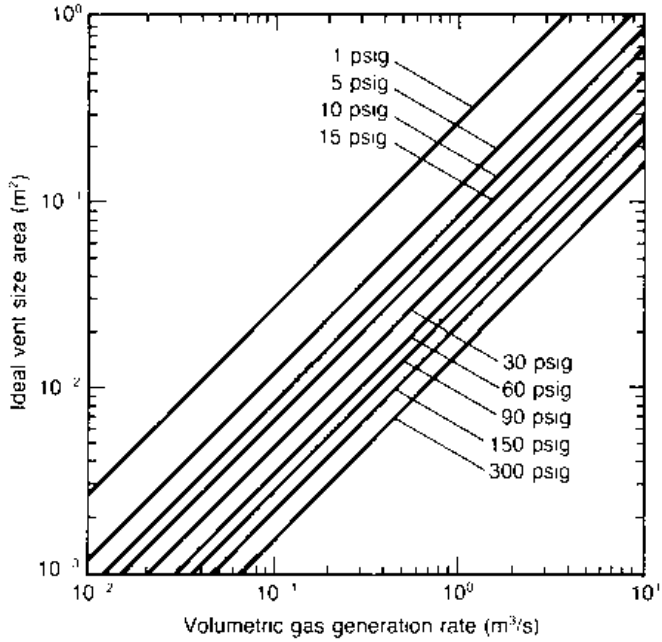


Figure 17.50 *Venting of chemical reactors: nomograph for vent sizing for a gassy system (Fauske, Grolmes and Clare, 1989) (Courtesy of the American Institute of Chemical Engineers)*

$$A = \frac{(Q_g + Q_v)\rho_l(1-\alpha)}{G} \qquad [17.19.12]$$

where Q_g is the peak volumetric gas evolution rate (m^3/s) and Q_v is the peak volumetric vapour evolution rate (m^3/s).

Tempered hybrid systems may be treated as tempered systems, provided it is assured that the system really is tempered and will continue to be so until the reaction is complete.

Effective tempering can occur well before the peak volume generation rate.

Leung and Fauske (1987) have described the application of Leung's method to a tempered hybrid system.

17.19.9 Bench-scale equipment

As already described, the bench scale equipment may be used in three different ways: (1) to determine the required flow, (2) to determine the parameters for the calculation of flow and (3) to effect direct scale-up.

There are certain pitfalls in the use of bench scale apparatus. These are described in the accounts given by Fauske and co-workers together with the precautions necessary to avoid them (Fauske, 1984a, 1985a).

The inaccuracies due to high thermal inertia, or ϕ value, are minimized in the DIERS apparatus by its design.

The viscosity of the reaction mass is often not known and the possibility may exist that the vent flow will be not turbulent but laminar. This can be checked by measuring the vent flow in the bench scale test.

An important feature for both vapour pressure and gassy systems is the effect of reactor height, since the superficial velocity is a function of height and is therefore much larger at the full scale that at bench scale.

There is a possibility that with vapour pressure systems the volumetric vent flow may be high at bench scale because the flow is all vapour rather than two-phase and/or because it is non-equilibrium due to insufficient relaxation length.

With a vapour pressure or hybrid tempered system it is necessary to ensure that the system remains tempered throughout by running the reaction to term. It is also necessary to confirm that there are no further reaction exotherms.

17.19.10 Direct scale-up

A method for direct scale-up from the bench scale apparatus, applicable only to vapour pressure systems, has been described by Fauske (1984c). An experiment is performed with bottom venting and with a vent line long enough to ensure equilibrium flow ($L \geq 0.1\,m$) and the adiabatic rise time Δt_A and vessel emptying time Δt_E are determined. The vent area of the full scale reactor is then obtained as

$$A_{LS} = A_T \frac{\Delta t_E}{\Delta t_A} \frac{V_{LS}}{V_T} \qquad [17.19.13]$$

where A is the vent area (m^2), Δt_A is the measured adiabatic rise time (s), Δt_E is the measured vessel emptying time (s) and the subscripts LS and T denote large scale and test, respectively.

For gassy systems Fauske (1985a) states that use of top venting on the bench scale apparatus and direct scale-up on a vent area/reactor volume basis is suitable.

17.19.11 Validation

The DIERS project and the subsequent work have included a number of validation exercises.

The *Technology Summary* describes the validation of the method for vapour pressure systems against incidents described by Burchett (1980) and a large-scale styrene/ethylbenzene test.

The Burchett incidents involved runaways of chloroprene reactions. The first was in a 11 355 litre vessel with a 0.010 m bursting disc set at 0.3 MPa and an equivalent sized vent pipe, which vented safely. The second incident was in a 7570 litre vessel with a bursting disc of the same size, but set at 0.61 MPa, which resulted in vessel rupture. On the assumption of churn turbulent flow it is predicted that both vessels should vent safely, whilst on the assumption of homogeneous venting (homogeneous vessel behaviour and homogeneous equilibrium vent flow), the prediction is that the first vessel would vent safely but that the second would not, which is what happened.

These incidents are also treated by Fauske (1984c).

The method for vapour pressure systems has also been compared by Fauske (1984a) with the results from a number of methods, as described in Section 17.19.2.

Test data for some 55 systems, tempered and non-tempered, have been given by Leung and Fauske (1987). They give comparisons with the vent area predicted by the FIA method.

Fauske (1989a) gives some experimental data obtained on both bench scale and large scale equipment, as shown in Table 17.20. The table shows the measured mass velocities together with the values obtained by calculation from Equation 17.18.12 and by scale-up.

Kirch, Magee and Stuper (1990) compare the DIERS method with a method used by their company based on scale-up using a constant ratio of the vent area to the charge volume.

17.19.12 Illustrative examples

A variety of illustrative examples are given in the *Technology Summary* and by Fauske and co-workers.

The main examples in the *Technology Summary* are in Appendix D, which gives calculations for determination of the flow regime into the vent and of the mass velocity with homogeneous flow and with partial vapour disengagement for a nozzle vent and for a long line vent.

Leung (1986b) gives two examples: one is the styrene polymerization described by Huff (1982b) and the other a phenolic reaction described by the BPF (1979) and Booth *et al.* (1980).

Leung and Fauske (1987) deal with the following types of system: type Ia, a vapour pressure, tempered system; type Ib, a gassy tempered system; and type II a non-tempered system. These are illustrated by a phenol–formaldehyde reaction, a hydrogen peroxide reaction and a hypothetical gassy reaction, respectively. They give illustrative examples for all three cases.

Examples illustrating the application of the methods to check existing plant are given by Fauske (1988a), who deals with a vapour pressure system for three cases: (a)

Table 17.20 *Venting of chemical reactors: some experimental data, bench-scale and large scale, on the venting of runaway reactions of polystyrene/ethylbenzene (Fauske, 1989a) (Courtesy of the American Institute of Chemical Engineers)*

Vent diameter (m)	*Vent length/ vent diameter*	*Stagnation conditions*				*Mass velocity* ($kg/m^2\,s$)		
		Pressure (Pa)	*Temperature* (K)	$\Delta P/\Delta T$ (Pa/°C)	*Viscosity* (kg/m s)	*Measured*	*Calculated*[a]	*Scaled up*
0.0525	100	5.8×10^5	498	11.35×10^5	0.45	1296	974	1258
0.0525	175	5.3×10^5	493	10.58×10^5	0.50	407	496	452
0.00457	100	5.1×10^5	480	10.14×10^5	0.55	71	55	
0.00457	175	5.03×10^5	490	10.14×10^5	0.55	33	31	

[a] Equation 17.18.12.

Table 17.21 *Venting of chemical reactors: illustrative calculation of vent sizing for reactor with vapour pressure system (after Fauske and Leung, 1985) (Courtesy of the American Institute of Chemical Engineers)*

A Scenario

Liquid specific heat $C = 2520\,kJ/kg\,K$
Initial reaction mass $m_o = 5000\,kg$
Reactor volume $V = 7.78\,m^3$
Set pressure $P_s = 5.15 \times 10^5\,Pa$
Set temperature $T_s = 491\,K$
$dP/dT = 8246\,Pa/K$
$(dT/dt)_s = 0.25\,°C/s$
$(dT/dt)_m = 0.33\,°C/s$
Mass velocity $G = 3640\,kg/m^2\,s$

B Vent sizing

Using Equation 17.20.19:

$$q = \frac{1}{2}2520(0.25 + 0.33) = 0.735\,kW/kg$$

Using Equation 17.20.18

$$A = \frac{5000 \times 735}{3640\left[\left(\frac{7.78}{5000}(491 \times 8246\right)^{\frac{1}{2}} + (2520 \times 11.6)^{\frac{1}{2}}\right]^2} = 0.016\,m^2$$

without vapour disengagement, (b) with disengagement and (c) check for potential viscosity effect (none found).

Fauske and Leung (1985) describe a study of the reaction runaway for an 80% styrene/20% ethylbenzene reaction which combines elements of validation and illustration. This system is a vapour pressure system and is foamy. The mass velocity was calculated from Equation 17.18.5, which requires no experimental data. The vent area was obtained from the model of Leung, Equation 17.20.18 with its supporting Equation 17.20.19, described below. This requires the self-heat rates at the set and turnaround temperatures. The bench scale apparatus was used to obtain these self-heat rates. It was also used to check the mass velocity determined from Equation 17.18.5. This agreed within 10% confirming the validity of Equation 17.18.5 which assumes turbulent flow.

Estimates of vent size were made for a range of overpressures using Equation 17.20.18. Estimates were also made using SAFIRE. There was excellent agreement between the two.

Table 17.21 shows the calculations given by the authors for the vent area using Equation 17.20.18 for this case.

In addition, a kinetic model for this reaction, given by Husain and Hamilec (1978), was used to predict the temperature and pressure profiles of the reaction. The predictions agreed well with the profiles measured in the bench scale apparatus.

17.19.13 Safety factors

Whatever method of vent sizing is used, a safety factor should be applied, having regard to the accuracy of the method itself and of the data used.

There is relatively little guidance given on this by Fauske and co-workers or by DIERS, but the problem has been discussed by Duxbury and Wilday (1990). These authors describe several methods for vent sizing

and mention certain safety factors. The safety factor to be applied is specific to the particular method and in each case the safety factor should be applied before a choice is made between the methods.

Safety factors are discussed further in Section 17.21 and Appendix 13.

17.20 Venting of Reactors and Vessels: Leung Model

Another model for vent sizing both of reactors and of storage vessels which has found wide acceptance has been given by Leung (1986b).

The model gives relations for vent sizing. The equations for vent area contain the vent flow mass velocity, but the model may be regarded as independent of the vent flow correlation used. The author does, however, state his own homogeneous equilibrium model (Leung, 1986a).

The model applies to vapour pressure systems, which give the tempering effect. It includes relations for the following cases:

(1) reactors –
   (a) homogeneous venting,
   (b) all vapour or all liquid venting;
(2) storage vessels –
   (a) homogeneous venting,
   (b) all vapour or all liquid venting.

The basic relations of the model and the treatments of these cases are now described.

17.20.1 Elementary relations

The unsteady-state mass and energy balances for the vessel, reactor or storage vessel, are

$$\frac{\mathrm{d}(\rho V)}{\mathrm{d}t} = -W \qquad [17.20.1]$$

$$\frac{\mathrm{d}(\rho V u)}{\mathrm{d}t} = Q - W\left(u_1 + \frac{P}{\rho_1}\right) \qquad [17.20.2]$$

where P is the absolute pressure, Q is the heat generation or input rate, T is the absolute temperature, u is the specific internal energy, V is the volume of the vessel, W is the mass flow from the vessel, ρ is the density and the subscript 1 denotes vent inlet. Combining Equations 17.20.1 and 17.20.2 leads to

$$\rho V \frac{\mathrm{d}u}{\mathrm{d}t} = Q - W\left(u_1 - u + \frac{P}{\rho_1}\right) \qquad [17.20.3]$$

But

$$m = \rho V \qquad [17.20.4]$$

$$\rho = 1/v \qquad [17.20.5]$$

$$v = v_\mathrm{f} + x v_\mathrm{fg} \qquad [17.20.6]$$

$$u = u_\mathrm{f} + x u_\mathrm{fg} \qquad [17.20.7]$$

$$h = u + Pv \qquad [17.20.8]$$

where h is the specific enthalpy, h_fg is the latent heat of vaporization, m is the mass of material in the vessel, x is the mass fraction of the vapour, or quality, and the subscript f denotes liquid and fg liquid–vapour transition. Then from Equations 17.20.3 and 17.20.4–17.20.8

$$m\left(\frac{\mathrm{d}u_\mathrm{f}}{\mathrm{d}T} + x\frac{\mathrm{d}u_\mathrm{fg}}{\mathrm{d}T}\right)\frac{\mathrm{d}T}{\mathrm{d}t} = Q - W[(x_1 - x)u_\mathrm{fg} + Pv_1] - mu_\mathrm{fg}\frac{\mathrm{d}x}{\mathrm{d}t} \qquad [17.20.9]$$

Noting that $\mathrm{d}V/\mathrm{d}t = 0$, Equation 17.20.1 may be expressed as

$$m\frac{\mathrm{d}}{\mathrm{d}t} = Wv \qquad [17.20.10]$$

With constant phase properties Equation 17.20.10 becomes

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{Wv}{mv_\mathrm{fg}} \qquad [17.20.11]$$

For an ideal gas and a nearly full vessel a practical approximation is obtained by reformulating the left-hand side of Equation 17.20.9 to give

$$mx\left\{(C_\mathrm{pg} - R) + (1 - x)\left[C_\mathrm{pf} - T\left(\frac{\mathrm{d}v_\mathrm{f}}{\mathrm{d}T}\right)\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)\right]\right\}\frac{\mathrm{d}T}{\mathrm{d}t}$$

$$= Q - W[(x_1 - x)u_\mathrm{fg} + Pv_1] - mu_\mathrm{fg}\frac{\mathrm{d}x}{\mathrm{d}t} \qquad [17.20.12]$$

where C_pf is the specific heat at constant pressure of the liquid, C_pg is the specific heat at constant pressure of the vapour and R is the gas constant.

Then from Equations 17.20.11 and 17.20.12

$$mC\frac{\mathrm{d}T}{\mathrm{d}t} = Q - Wh_\mathrm{fg}\left(x_1 + \frac{v_\mathrm{f}}{v_\mathrm{fg}}\right) \qquad [17.20.13]$$

where C is the specific heat at constant volume of the liquid, the assumption being made that $C_\mathrm{p} \approx C_\mathrm{vf} \approx C$.

Equation 17.20.13 is used to derive expressions for the vent area for the specific cases.

The vent area is given by the relation

$$W = GA \qquad [17.20.14]$$

where A is the area of the vent and G is the mass velocity of the vent flow.

17.20.2 Reactor venting: homogeneous venting

For a reactor with homogeneous venting

$$x_1 = x \qquad [17.20.15]$$

$$v_1 = v = V/m \qquad [17.20.16]$$

Hence Equation 17.20.13 becomes

$$mC\frac{\mathrm{d}T}{\mathrm{d}t} = mq - GA\frac{V}{m}\frac{h_\mathrm{fg}}{v_\mathrm{fg}} \qquad [17.20.17]$$

where q is the heat release rate per unit mass.

On certain assumptions and utilizing Equations 17.20.1 and 17.20.14, Equation 17.20.17 can be integrated to yield

$$A = \frac{m_\mathrm{o} q}{G\left[\left(\frac{V}{m_\mathrm{o}}\frac{h_\mathrm{fg}}{v_\mathrm{fg}}\right)^{\frac{1}{2}} + (C\,\Delta T)^{\frac{1}{2}}\right]^2} \qquad [17.20.18]$$

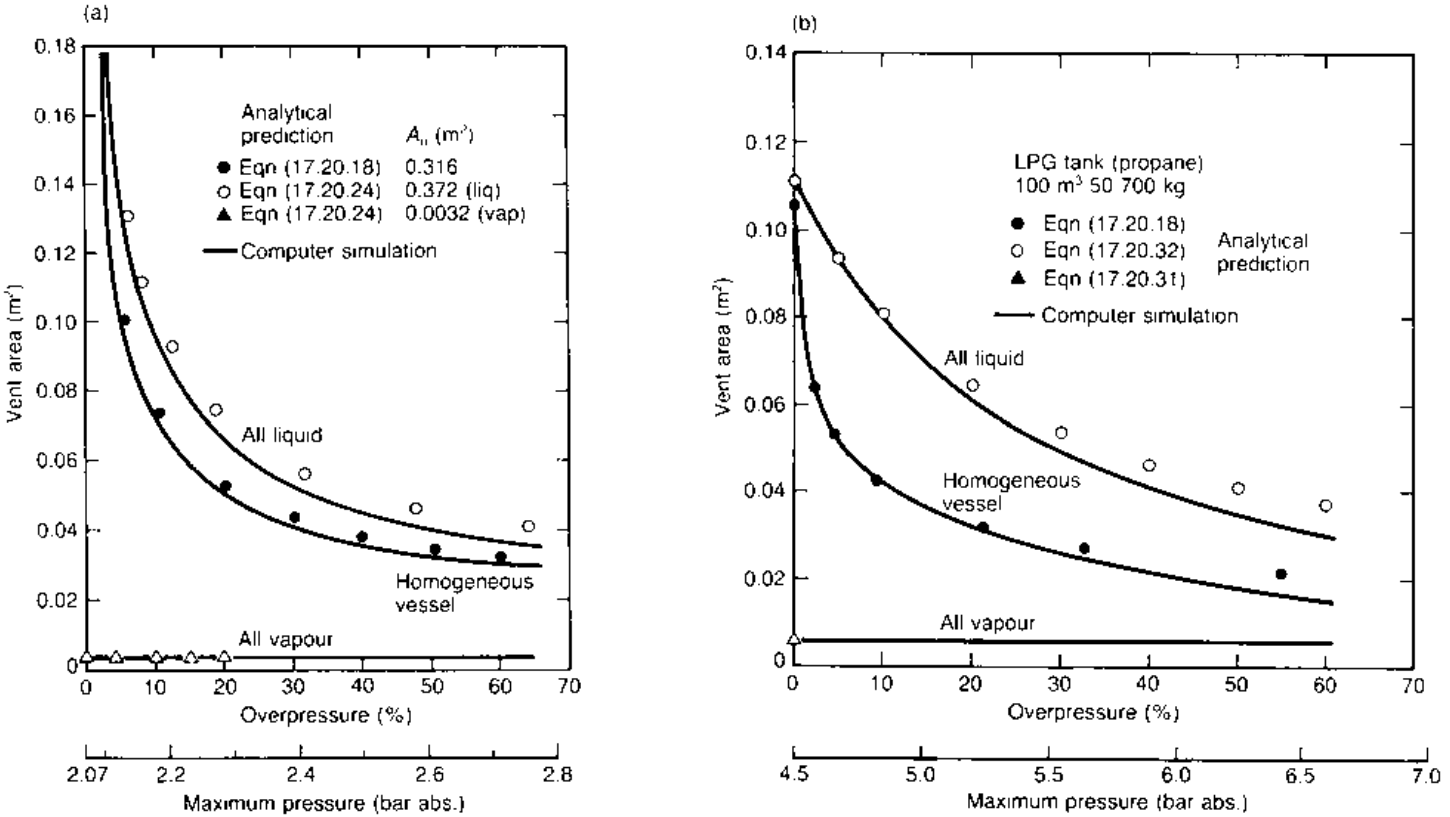


Figure 17.51 *Venting of chemical reactors: effect of vent fluid phase on vent area (Leung, 1986b): (a) phenolic reaction and (b) propane storage vessel (Courtesy of the American Institute of Chemical Engineers)*

with

$$q = \frac{1}{2}C\left[\left(\frac{dT}{dt}\right)_s + \left(\frac{dT}{dt}\right)_m\right] \quad [17.20.19]$$

where m_o is the initial mass in the vessel and the subscripts m and s denote peak pressure or temperature and relief set pressure, respectively.

For zero overpressure, Equation 17.20.18 reduces to

$$A_o = \frac{m_o q_s v_{fg}}{G v h_{fg}} \quad [17.20.20]$$

where A_o is the area of the vent for zero overpressure.

17.20.3 Reactor venting: all vapour or all liquid venting

For a reactor with all vapour or all liquid venting

$$v_i = v_g \quad \text{All vapour venting} \quad [17.20.21]$$

$$= v_f \quad \text{All liquid venting} \quad [17.20.22]$$

where the subscript i denotes phase (either g or f). Hence Equation 17.20.13 becomes

$$mC\frac{dT}{dt} = mq - GAv_i\frac{h_{fg}}{v_{fg}} \quad [17.20.23]$$

This equation can be integrated to give

$$T_m - T_s = \frac{m_o q}{GAC}\left(1 - \frac{A}{A_o}\right) + \frac{v_i h_{fg}}{v_{fg} C}\ln\left(\frac{A}{A_o}\right) \quad [17.20.24]$$

with

$$A_o = \frac{m_o q_s v_{fg}}{G v_i h_{fg}} \quad [17.20.25]$$

For zero overpressure, Equation 17.20.24 reduces to the correct limit with $A = A_o$.

17.20.4 Storage vessel venting: homogeneous venting

For a storage vessel with homogeneous venting

$$Q = Q_T \quad [17.20.26]$$

where Q_T is the total heat input. Hence Equation 17.20.13 becomes

$$mC\frac{dT}{dt} = Q_T - GA\frac{V}{m}\frac{h_{fg}}{v_{fg}} \quad [17.20.27]$$

This equation can be integrated to give

$$T_m - T_s = \frac{Q_T}{GAC}\left[\ln\left(\frac{m_o}{V}\frac{Q_T}{GA}\frac{v_{fg}}{h_{fg}}\right) - 1\right] + \frac{V h_{fg}}{m_o C v_{fg}} \quad [17.20.28]$$

For zero overpressure, Equation 17.20.28 reduces to the correct limit

$$A_o = \frac{Q_T m_o v_{fg}}{G V h_{fg}} \quad [17.20.29]$$

A comparison of the reactor and storage vessel cases may be made by setting $Q_T = m_o q$ and $v = V/m_o$. Equations 17.20.20 and 17.20.29 are then equivalent.

Leung refers to the work of Forest (1985), who has given a relationship which is equivalent to, but differs slightly in form from, Equation 17.20.29 and which has found application to the fire exposure of storage vessels.

17.20.5 Storage vessel venting: all vapour or all liquid venting

For a storage vessel with all vapour or all liquid venting, utilizing again $v_i = v_g$ and $v_i = v_f$ for the two cases, respectively, Equation 17.20.13 becomes

$$mC\frac{dT}{dt} = Q_T - GAv_i\frac{h_{fg}}{v_{fg}} \quad [17.20.30]$$

For all vapour venting, it is assumed that the design is for no overpressure. The right hand side of Equation 17.20.30 is set to zero to yield

$$A_o = \frac{Q_T v_{fg}}{G v_g h_{fg}} \quad [17.20.31]$$

For all liquid venting, it assumed that temperature turnaround occurs at a point where the vessel contains 10% of its initial inventory. Equation 17.20.30 can then be integrated to yield

$$A = \frac{Q_T}{G\left(v_f\frac{h_{fg}}{v_{fg}} + \frac{C\,\Delta T}{e}\right)} \quad [17.20.32]$$

where e is the base of natural logarithms (= 2.303).

For zero overpressure, Equation 17.20.32 reduces to

$$A_o = \frac{Q_T v_{fg}}{G v_f h_{fg}} \quad [17.20.33]$$

17.20.6 Illustrative examples

Leung gives illustrations of the effect of these different assumptions on the vent areas required for venting of reactors and storage vessels. His results are shown in Figure 17.51. Figure 17.51(a) shows an example for a reactor with a phenolic reaction and Figure 17.51(b) one for an LPG storage vessel.

17.21 Venting of Reactors and Vessels: ICI Scheme

Accounts of the approach to vent sizing for reactors used in ICI have been given by Duxbury and Wilday (1987, 1989, 1990). These provide a useful insight into the way in which one company has integrated the DIERS methods with other methods. The description given here is based unless otherwise stated on the most recent paper. The basic notation is the same as that used in Section 17.20.

17.21.1 Set pressure and overpressure

An effective, or redefined, set pressure is defined as the pressure at which the relief device is known to be fully open. For a bursting disc this will correspond to the nominal set pressure plus any tolerances or to the maximum specified bursting pressure. For a safety valve the redefined set pressure will often be 10% above the nominal set pressure. Similarly, an effective, or redefined, overpressure is defined as the difference between the redefined set pressure and the maximum pressure attained during the venting process. These definitions differ from those in some standards, including the British Standards, but are implicit in much of the DIERS work.

Table 17.22 *Venting of chemical reactors: some vent sizing methods (after Duxbury and Wilday, 1989) (Courtesy of the American Institute of Chemical Engineers)*

		Reference
A	All gas/vapour venting	Duxbury (1980)
B	Two-phase venting to maintain pressure constant	Duxbury (1980); Duxbury and Wilday (1989)
C	Modified Boyle method	Boyle (1967); Duxbury (1980)
D	Vent area/vessel volume scale-up	Duxbury (1980)
E	Full dynamic simulation	Duxbury (1980); Huff (1984a); Grolmes and Leung (1985); Klein (1986)
F	Huff's pseudo-steady-state method	Duxbury (1980)
G	Fauske short-form equation	Fauske (1984a)
H	Fauske nomograph	Fauske (1984b)
J	Leung long-form equation	Fauske and Leung (1985); Leung (1986b); Leung and Fauske (1987)
K	Fauske revised method	Fauske (1987a,b)
L	Fauske revised nomograph for tempered systems	Fauske, Grolmes and Clare (1988)
M	Fauske nomograph for gassy/untempered systems	Fauske, Grolmes and Clare (1988)
N	Leung's method taking account of disengagement	Leung (1987)
P	Wilday's method for homogeneous venting until disengagement	Duxbury and Wilday (1989)
Q	Wilday's method for homogeneous venting at high overpressure	Duxbury and Wilday (1989)

17.21.2 Vent sizing methods

Duxbury and Wilday (1989) give a list of vent sizing methods. This list is given in Table 17.22. All the methods, except method M, may, in appropriate circumstances, be applicable to vapour pressure systems.

17.21.3 Vent flow

The methods used for estimation of vent flow described by Duxbury and Wilday (1990) are those applicable to vapour pressure systems. Use is made of the ERM given in Equations 17.18.4 and 17.18.5 where it is applicable. Where it is not applicable, a fluid flow code is utilized.

If venting is through a safety valve, it is usually sized using the ERM, but where the pipework is significant, a fluid flow code is used to check pressure drops upstream and downstream. If venting is through a bursting disc the vent line flow correction factor provided for use with the ERM model is used for preliminary estimates, but since it is applicable only to a vent line with constant diameter and no static head changes, the final calculation is done using the fluid flow code.

17.21.4 Vapour pressure systems

For vapour pressure systems, use is made of Leung's method, as given in Equation 17.20.18. The assumption of homogeneous equilibrium flow is safe and generally realistic and the method gives a safe and usually acceptable vent size.

An alternative and sometimes more convenient formulation of Equation 17.20.18,

$$A = \frac{m_o q}{G\left[\left(\frac{V}{m_o} T_m \left(\frac{dP}{dT}\right)_m\right)^{\frac{1}{2}} + (C\,\Delta T)^{\frac{1}{2}}\right]^2} \qquad [17.21.1]$$

where subscript m denotes the mean value between the set pressure (as redefined) and the maximum allowable pressure.

The authors term this the Leung long-form equation (method J).

Where it is suitable, use is also made of Fauske's method for vapour pressure systems. This is the enhanced method which takes account of vapour disengagement, as given in Equation 17.19.6 (method K).

The Fauske method is used in conjunction with the Leung method. In the first instance it provides a check. If the two methods are significantly different, the calculations are reviewed. A significantly smaller answer from the Fauske method would not be accepted without rechecking the conditions for applicability and checking that the vent is large enough for all vapour venting.

Appropriate safety factors are then applied for each method. One safety factor is associated with the uncertainties in the data. If 'safe' values have been used, this safety factor is taken as unity. Another safety factor is associated with uncertainties in the vent flow calculation. Typically this safety factor is in the range 1–2 on flow, or area, the larger values being typical for two-phase flow in long lines. A detailed treatment of safety factors by Duxbury is given in Appendix 13.

The vent sizes from the two methods so obtained are then compared. The final vent size is taken as the smaller of the two.

This hand calculation method is generally both convenient and sufficient. The main effort required is associated with definition of the worst case conditions and gathering of data rather than with the vent sizing as such. Other methods are used only if both methods are judged inapplicable or if the vent size obtained is unacceptably large.

Before applying either method it is necessary to review its applicability.

The DIERS documentation states that Leung's method is limited to effective overpressures of 0–50%. It tends in fact to overestimate the vent size for higher overpressures. In order to permit integration, the model assumes constant various quantities such as physical and thermodynamic properties, heat evolution rate and vent capacity per unit area. The values of the parameters at the set pressure and maximum allowable pressure may be compared in order to assess the error and the extent to which the model may tend to oversize the vent.

The Fauske method is based on the ERM with a correction factor for vent line length. It is limited to overpressures in the range 10–30% and to turbulent flow.

In most cases the Fauske method is used without taking vapour disengagement into account and thus with α_d set equal to unity.

For those cases where credit is to be taken for vapour disengagement, it is necessary to perform the following check. The Fauske method is regarded as potentially unsafe if early vapour disengagement occurs, which in this context means disengagement occurring before the pressure would otherwise have turned around during two-phase venting. The method is therefore used only if disengagement would have occurred after the turnaround. Duxbury and Wilday (1989) have derived the following criterion which must be satisfied for safe use of the method:

$$q < \frac{GAh_{fg}v_f^2}{Vv_{fg}(1-\alpha_d)^2} \qquad [17.21.2]$$

where α_d is the void fraction at disengagement.

17.21.5 Vapour pressure systems: enhancements of Wilday

Duxbury and Wilday (1989) describe two enhancements to the Leung method (method J) for vapour pressure systems developed by Wilday.

The first of these (method P) is for the case where there is vapour disengagement part-way through the venting, with two-phase flow in the early part and all vapour flow in the later part and, further, the disengagement occurs before the pressure would have turned around during homogeneous venting. It is based on an adaptation of Leung's model. The following additional equations may be written:

$$m = V(1-\alpha)/v_f \qquad [17.21.3]$$

and, neglecting the vapour phase mass,

$$m_o = V(1-\alpha_o)/v_f \qquad [17.21.4]$$

where α is the void fraction and α_o is the initial void fraction.

Then combining Equations 17.20.1 and 17.20.17 of Leung and Equations 17.21.3 and 17.21.4 gives

$$A = \frac{qV(\alpha-\alpha_o)}{Gv_f\left(\frac{h_{fg}v_f(\alpha-\alpha_o)}{v_{fg}(1-\alpha_o)(1-\alpha)} + C\,\Delta T\right)} \qquad [17.21.5]$$

This method is valid only if vapour disengagement occurs before the point at which pressure turnaround would have occurred in homogeneous venting. Otherwise it gives too small a vent area and is unsafe. Before pressure turnaround the rate of temperature rise dT/dt in a vapour pressure system is positive, and hence from Equation 17.20.17

$$mq > GA\frac{V}{m}\frac{h_{fg}}{v_{fg}} \qquad [17.21.6]$$

which with Equation 17.21.3 gives the criterion

$$q > \frac{GAh_{fg}v_f^2}{Vv_{fg}(1-\alpha_d)^2} \qquad [17.21.7]$$

The second method given by Wilday (method Q) is based on Leung's model for homogeneous venting (method J). The assumption underlying this model is that the physical properties, heat release rate and mass velocity are constant. Wilday's method involves dividing the available pressure range into stages in which it is more reasonable to assume these quantities constant. Again criteria are given for the applicability of the method.

17.21.6 Gassy systems

For gassy systems, the principal method of vent sizing is based on maintaining the pressure constant.

The vent is sized so that the two-phase volumetric flow at the maximum allowable pressure exceeds the peak volumetric gas generation rate at that pressure. The vent sizing equation given is Equation 17.19.9. An appropriate safety factor should then be applied as described in Section 17.21.4.

Use of the Fauske nomograph for gassy systems, Figure 17.50, would be limited to making preliminary estimates. Mention is also made of the treatment of gassy systems by Leung and Fauske (1987).

For gassy systems, use may also be made of direct scale-up, which may well give a smaller vent area due to early loss of reactant. Alternatively, the vent may be sized by simulation using a numerical model. Again, for the reason just given, this may give a smaller vent.

A note of caution is sounded in that for gassy systems it may be unsafe to make the assumption of homogeneous two-phase venting. This assumption gives the maximum rate of emptying the reactor. If some disengagement occurs, liquid will remain in the reactor and the peak gas generation rate may be reached. A larger vent may then be required than for the relatively low gas generation rate occurring earlier in the relief process.

17.21.7 Hybrid systems

For hybrid systems, the appropriate method depends on whether the reaction is tempered. For tempered hybrid systems, it is first necessary to check that the reaction will remain tempered throughout. Reference is made to the treatment of such systems by Leung and Fauske (1987).

Untempered hybrid systems usually have to be treated as gassy systems. Use would be made of Equation 17.19.9 provided the vent size obtained is not excessive. The flow Q_g to be used in that equation is the total volumetric evolution of both gas and vapour.

17.21.8 Illustrative examples

The illustrative examples of vent sizing for a vapour pressure system and a gassy system given by Duxbury and Wilday (1990) are summarized in Table 17.23.

Table 17.23 *Venting of chemical reactors: illustrative calculations of vent size for reactors with (A) a vapour pressure system and (B) a hybrid system treated as a gassy system (after Duxbury and Wilday, 1990) (Courtesy of the Institution of Chemical Engineers)*

A Example of vapour pressure system

	Reactor pressure (bara)		
	3.2	4.2	Average
Bubble point temperature (°C)	110	120.5	115.3
Liquid density (kg/m^3)	847	835	841
Vapour density (kg/m^3)	3.75	4.62	4.19
Liquid specific heat (J/kg K)	1960	1960	1960
Latent heat (J/kg)	6.749×10^5	6.630×10^5	6.690×10^5
dP/dT (Pa/K)	8300	9500	
v_{fg} (m^3/kg)	0.2655	0.2153	0.2404
Heat release rate (W/kg)	1150	1660	1405

Reactor volume = 2.1 m^3
Reaction mass = 1500 kg
Vessel design pressure = 2.86 barg
Bursting disc pressure[a] = 3.20 bara
Vent line length/diameter = 200

Maximum allowable pressure = $1.1 \times 2.86 = 3.15$ barg = 4.16 bara
Allowable overpressure = $4.16 - 3.20 = 0.96$ bar

For mass velocity at 3.2 bara, using Equation 17.18.9 with a correction factor $F = 0.65$:

$$G = 0.65 \times 8300 \times \left(\frac{383}{1960}\right)^{\frac{1}{2}} = 2385 \text{ kg/m}^2 \text{ s}$$

Alternatively, using Equation 17.18.4:

$$G = 0.65 \times \frac{6.749 \times 10^5}{0.2655}\left(\frac{1}{1960 \times 383}\right)^{\frac{1}{2}} = 1907 \text{ kg/m}^2 \text{ s}$$

Since the difference between these two estimates is appreciable, a rigorous fluid flow method was used to obtain the following estimate:

$G = 2264$ kg/m^2 s

A similar calculation for the mass velocity at 4.16 bara gave

$G = 2688$ kg/m^2 s

The average of these two mass velocities is:

$G = (2264 + 2688)/2 = 2476$ kg/m^2 s

Applying a safety factor of 2 on mass velocity:

$G = 2476/2 = 1238$ kg/m^2 s

Allowable temperature rise $\Delta T = 120.5 - 110 = 10.5$ K

(1) Using Leung's method, Equation 17.20.18:

$$A = \frac{1500 \times 1405}{1238\left[\left(\frac{2.1 \times 6.690 \times 10^5}{1500 \times 0.2404}\right)^{0.5} + (1960 \times 10.5)^{0.5}\right]^2} = 0.04 \text{ m}^2;\ D_v = 0.226 \text{ m}$$

Alternatively, using Equation 17.21.1:

$$\left(\frac{dP}{dT}\right)_m = \frac{(4.16 - 3.2) \times 10^5}{120.5 - 110} = 9143 \text{ Pa/K}$$

Table 17.23 *Continued*

A Example of vapour pressure system – continued

$$A = \frac{1500 \times 1405}{1238\left[\left(\frac{2.1 \times 388 \times 9143}{1500}\right)^{0.5} + (1960 \times 10.5)^{0.5}\right]^2} = 0.0372\ \text{m}^2;\ D_\text{v} = 0.218\ \text{m}$$

(2) Using Fauske's method, Equation 17.19.6; assume no vapour disengagement so that $\alpha_\text{D} = 1$

$$\left(\frac{\text{d}T}{\text{d}t}\right)_\text{s} = \left(\frac{q_\text{m}}{C_\text{m}}\right)_\text{s} = \frac{1150}{1960} = 0.587\ \text{K/s}$$

For vent line $L/D = 200$ with a correction factor $F = 0.65$

$$A = \frac{1}{2}\frac{1500 \times 0.587}{0.65(383/1960)^{\frac{1}{2}} \times 0.96 \times 10^5}\frac{(1-\alpha_\text{o})}{(1-\alpha_\text{o})} = 0.016\ \text{m}^2$$

Applying a safety factor of 2 on vent area:

$A = 2 \times 0.016 = 0.032\ \text{m}^2;\ D_\text{v} = 0.202\ \text{m}$

The difference between the vent area given by Leung's method and that given by Fauske's method, after application of the safety factor of 2, is some 20%.

B Example of hybrid system treated as gassy system

Molecular weight of liquid	65
Liquid density at 95°C (kg/m^3)	800
Latent heat (J/kg)	2.76×10^5
Heat release rate (W/kg)	53
Temperature for peak reaction rate (°C)	95
Peak gas evolution rate (l/kg s)[b]	0.146
Reactor volume (m^3)	5.0
Reaction mass (kg)	3200
Maximum allowable pressure (bara)	4.8

From a separate calculation, the mass velocity, including the safety factor, is found to be 2400 kg/m^2 s:

$$\text{Vapour evolution rate} = \frac{3200 \times 53}{2.76 \times 10^5} = 0.614\ \text{kg/s}$$

Volumetric vapour evolution rate at 4.8 bara and 95°C:

$$= \frac{0.614}{65} \times 22.4 \times \frac{368}{273} \times \frac{1.013}{4.8} = 0.06\ \text{m}^3/\text{s}$$

Volumetric gas evolution rate at 4.8 bara and 95°C:

$$= 0.146 \times 10^{-3} \times 3200 \times \frac{368}{298} \times \frac{1.013}{4.8} = 0.122\ \text{m}^3/\text{s}$$

Liquid volume in reactor = 3200/800 = 4.0 m^3
Void fraction $\alpha = (5.0 - 4.0)/5.0 = 0.2$

Using Equation 17.19.9:

$$A = \frac{(0.060 + 0.122) \times 800(1 - 0.2)}{2400} = 0.0485\ \text{m}^2;\ D_\text{v} = 0.249\ \text{m}$$

[a] Maximum specified bursting pressure.
[b] Volume (l) measured at atmospheric pressure and 25°C.

17.22 Venting of Reactors: Relief Disposal

17.22.1 General considerations

The problem of reactor relief does not stop with the venting. There remains the question of the disposal of the vented materials, which is often not trivial. The engineering of relief disposal is therefore a topic in its own right. An account is given by Kneale (1984).

The legal requirement is that any venting should be to 'a safe place'. Discharge to atmosphere may meet this requirement, but such discharge is increasingly constrained.

The options for disposal are (1) discharge and dispersion, (2) destruction and (3) containment.

A full definition of the relief requirements is as important for the design of the disposal system as for that of the relief device itself. Cases which should be considered include cooling failure during normal reaction, runaway of reaction for other reasons, explosion due to runaway or thermal instability, fire, overpressure by gas and overfilling by liquid.

The relieving process may be violent, and all equipment connected to the relief device, however remotely, should be designed for the hydraulic and mechanical forces released. This includes not only the inlet and outlet lines to the device but vessel and line supports, foundations and foundation bolts, and building structures.

Some common causes of deficiencies in relief disposal systems include failure to allow for (1) the presence of another phase, (2) the presence of fine particles and (3) variation in emission with time.

A general strategy for relief disposal is shown in Figures 17.52 and 17.53. In general, any stream containing liquid or solid should not be discharged directly to the atmosphere. Gas containing any liquid and solid is treated or contained and treated later, whilst liquid is contained and treated later.

Gas should be discharged to atmosphere only if it can be dependably diluted below any flammable and/or toxic limits which have to be met. Relations for the dispersion of such discharges are given in Chapter 15.

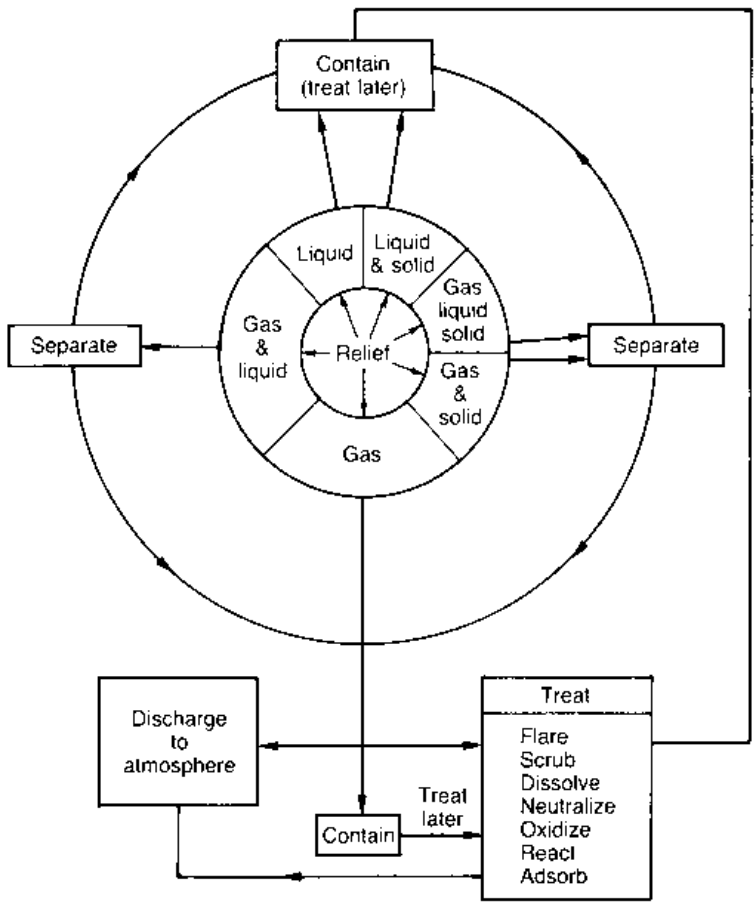


Figure 17.52 *Venting of chemical reactors: a taxonomy for relief disposal (Kneale, 1984) (Courtesy of the Institution of Chemical Engineers)*

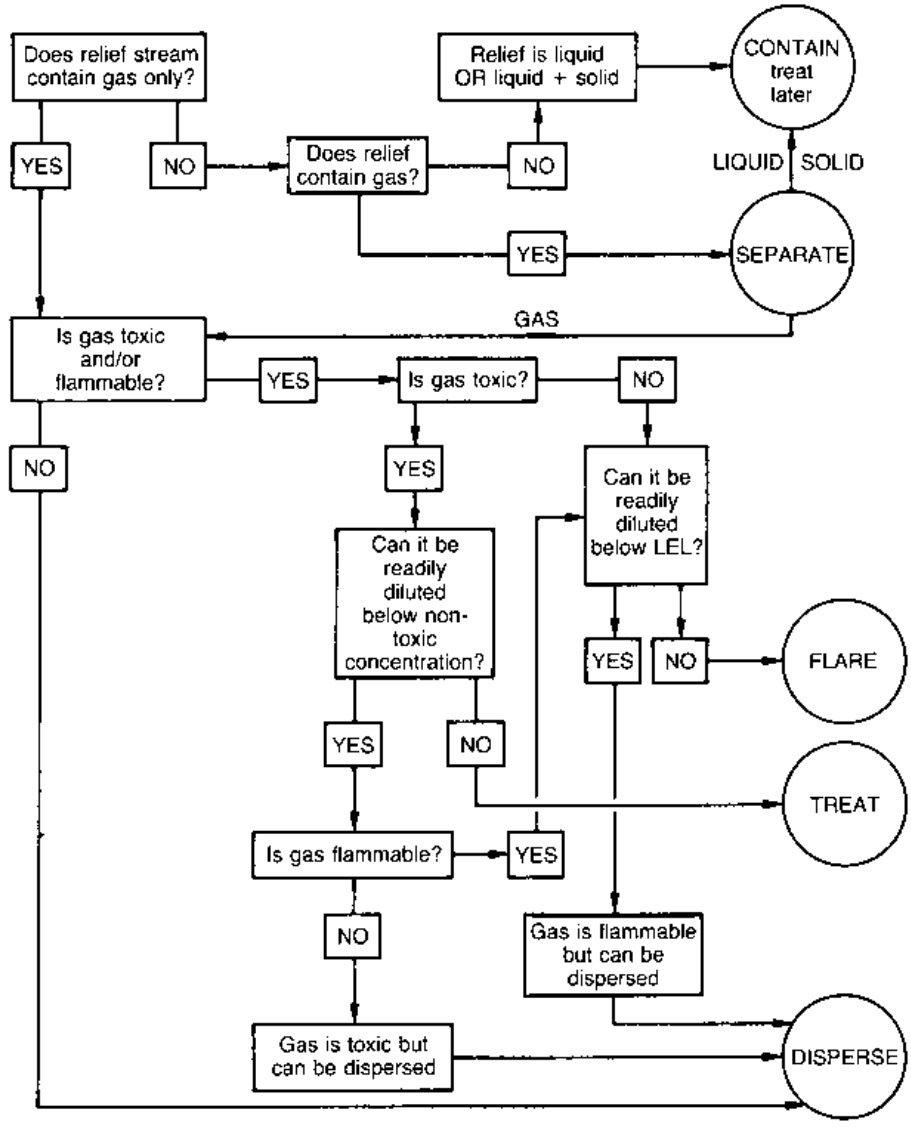


Figure 17.53 *Venting of chemical reactors: decision tree for relief disposal (Kneale, 1984). LEL, lower explosive limit (Courtesy of the Institution of Chemical Engineers)*

A study by Gerardu (1981) concluded that it is often simpler and safer to vent a pressure relief valve directly to the atmosphere, provided the hazard of ignition is allowed for.

It should be appreciated, however, that emergency discharge from a reactor is a transient process and that towards the end of this process the discharge will lose momentum and will tend to slump. This stage may well be the most hazardous, but also the most difficult to model.

Vents for the discharge of flammable gas to the atmosphere may be equipped with flame arresters, but where it is considered that the maintenance of such arresters cannot be guaranteed, they are often omitted.

Gas relieved is often sent to flare. The efficiency of destruction of combustible gas in a flare can be high; studies have shown combustion efficiencies well in excess of 99% (B.C. Davis, 1983).

An alternative means of dealing with gas is scrubbing. A major factor in the choice of system is whether the scrubber has the function of handling a normal process gas stream or of treating the emergency vent gas only. In the latter case the options are to run with liquid constantly circulating or to start up automatically when

venting starts. The cost of continuous circulation can be high, but it is not usual to rely on automatic start-up. Problems which can occur with scrubbers are boiling due to the high heat load imposed by the vent gas and carryover of spray.

Another option for handling the vented material is containment in a separate containment vessel, or catchtank. If the vent stream contains liquid or solid this is the appropriate design. Systems vary widely in complexity depending on the duty.

Apart from the cost, some problems which arise with containment are (1) reaction forces, (2) undetected leakage and (3) testing.

The reaction forces affect the containment vessel as they do the whole system. A leak occurring undetected across the relief system may fill the containment. Testing of the system requires careful thought.

A review of reaction forces has been given by Woods and Thornton (1967).

Studies have also been made on particular configurations. The forces on a system consisting of a reactor and a containment vessel separated by a bursting disc have been analysed by Porter (1982), and the interactive effects of bursting discs in a relief manifold by Beveridge and Jones (1984).

Relief venting can give rise to appreciable noise. Sonic flow across a pressure relief device is a very efficient noise generator. The tall vertical stack frequently used for dispersion tends to broadcast noise. Work by Shearer (1969) has shown that at a distance of 200 ft from a vent the noise level for a wide range of vent flows can be approximated by $25 \log_{10} V$, where V is the volumetric discharge (scfh). This was confirmed experimentally for a range of flows from 1 to 3000 scfh regardless of the initial pressure and temperature.

In view of the problems associated with venting, the alternative of containment within the reactor vessel should be considered. Kneale suggests that if vacuum collapse may occur, the vessel should preferably be designed for full vacuum. As far as concerns overpressure he proposes that the vessel design criterion should depend on the expected frequency of overpressure. If overpressure is expected to be a very rare event (say once in 100–10 000 years) the vessel may be designed for overstress beyond the yield point but within the bursting strength, whereas if it is expected more frequently (say once in 10–100 years), a stronger design is appropriate.

Kneale describes a number of incidents arising from reactor venting.

17.22.2 Two-phase relief flows

As already described, there has been growing appreciation, further stimulated by the DIERS work, that it is generally necessary that the relief disposal system for a reactor be capable of handling a two-phase vapour–liquid mixture.

Discussions of the implications of the need to dispose of two-phase mixtures and proposals for dealing with the problem have been given by Fauske (1986a, 1987b), H.G. Fisher (1991) and Fauske and Grolmes (1992).

In particular, more guidance has become available on knockout and catchment facilities.

17.22.3 Knockout drums and catchtanks

Treatments of the design of knockout drums and catchtanks are given in API RP 521: 1990, by the BPF (1979) and by Grossel (1986, 1990b). Further references are given in API RP 521.

API RP 521 gives a method for the sizing of a knockout drum which has been widely used. The basis is the provision of a cross-sectional area sufficient to ensure that the liquid droplets are not entrained in the vapour. The relation given is

$$u_d = 1.15\left(\frac{gd(\rho_l - \rho_v)}{C\rho_v}\right)^{\frac{1}{2}} \qquad [17.22.1]$$

where d is the particle diameter (m), g is the acceleration due to gravity (m/s^2), u_d is the dropout velocity (m/s), ρ_l is the density of the liquid (kg/m^3), ρ_v is the density of the vapour (kg/m^3) and C is the drag coefficient.

The drag coefficient C is given by Figure 17.54 in which

$$C(\mathrm{Re})^2 = 0.13 \times 10^8 \frac{\rho_v d^3(\rho_l - \rho_v)}{\mu^2} \qquad [17.22.2]$$

where μ is the viscosity of the gas (cP).

The selection and design of knockout drums and catchtanks has been described by Grossel (1986). There are a number of reasons why such devices may be needed. In a large proportion of cases the fluid entering the relief disposal system is a two-phase mixture, so that it is necessary to separate the vapour from liquid, and the liquid is hot and flammable, toxic and/or corrosive.

Grossel describes the following types of knockout and catchtank systems: (1) horizontal drum plus catchtank, typical of a refinery or petrochemical plant where space is not restricted; (2) cyclone separator plus catchtank, typical of chemical plant with less space available; (3) cyclone separator with integral catchtank, capable of handling a large vapour flow; (4) open tank; (5) quencher knockout drum/catchtank; (6) multi-input knockout drum/catchtank, with connections from a group of reactors; and (7) cyclone knockout drum. The first two of these systems are shown in Figure 17.55.

The open tank system may be used where the relief fluid contains an explosive mixture which it is judged better to release direct to atmosphere than to contain. The quencher knockout drum/catchtank system is used to condense out condensable vapour.

Principal factors in the design of such systems are a volume sufficient to hold the liquid and, for non-cyclone systems, a cross-sectional area sufficient to prevent liquid entrainment.

Expressions are given for the allowable vapour velocity u of the general form

$$u = k\left(\frac{\rho_l - \rho_v}{\rho_v}\right)^{\frac{1}{2}} \qquad [17.22.3]$$

where k is a constant.

For cyclone separators the design requirement may diverge somewhat from that for conventional applications. For a high flow, short duration emergency relief, some mist may be tolerable in the outlet, and a high vapour velocity may be acceptable.

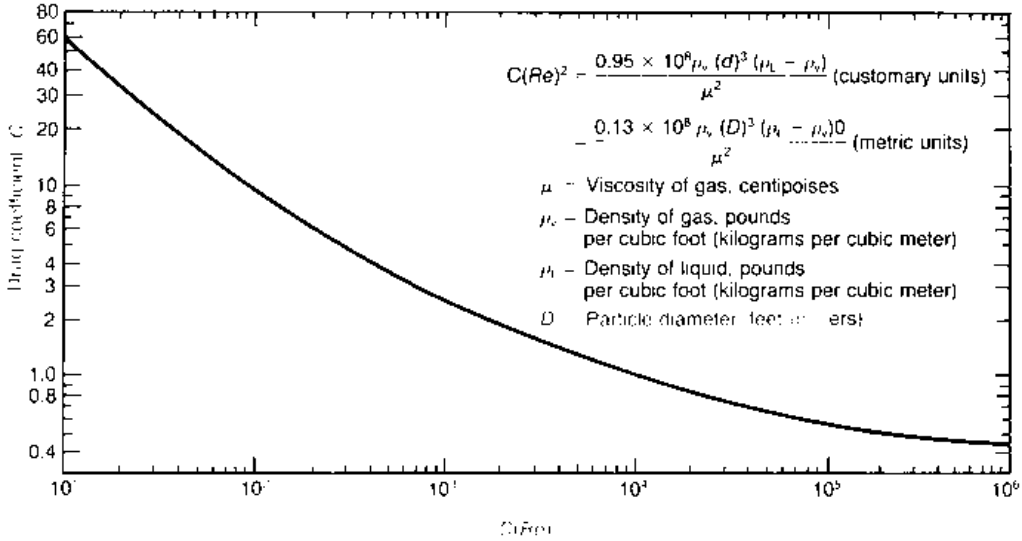


Figure 17.54 *Venting of chemical reactors: drag coefficient for knockout drum design (API RP 521: 1990) (Courtesy of the American Petroleum Institute)*

For quench tanks critical features are the suppression pool and quencher arm. The quench liquid should be compatible with the reaction mass to be quenched. The quantity of quench liquid in the pool should be sized so that its temperature rise after condensation of the condensable vapour does not exceed a suitable value. Grossel gives two further rules-of-thumb for the quench fluid. One is that the quantity should be some 2–3 times by volume that of the reaction mass and the other that the exit temperature of the vapour leaving the pool should be at least 10°C below its saturation temperature.

The design of the quench arm is also important. The device is prone to water hammer. Grossel gives several rules-of-thumb for this feature also. One is the limitation of the size of the holes to $\frac{1}{4}$in., since high hole velocities are desirable and large holes may result in water hammer. The other is that the hole area should be at least as great as the cross-sectional area of the inlet pipe from the relief device.

The relief pipework should be as short and as straight as possible. An account of the design of such piping has been given by Chambard (1980).

Consideration should be given to the pressure drop through the relief disposal train and its effect on the backpressure at the reactor vent.

Guidance is also given by Grossel on mechanical design of the catchtank. He suggests a minimum design pressure of 50 psig. The tank should be able to withstand a deflagration without rupture, though it may deform. Some companies use a design pressure of 125–150 psig.

The blowdown loads should be taken into account. Operation of a relief device creates reaction and impact forces. The reaction vessel is subject to reaction force and impact force due to slugs. Both reactor vessel and piping are affected by fluid acceleration wave forces. A quasi-steady state jet force occurs at the containment vessel.

Further, a quencher vessel is subject to impact force, condensation vibrations and final water hammer. The impact force is due to the impact of the fluid. The final water hammer occurs at the end of blowdown, when, if the reactor has been vented through a bursting disc, condensation can lead to a high flow back into the vent line and reactor vessel.

Grossel states that the catchtank should itself be provided with a bursting disc relieving into the catchtank vent line to handle continued reaction and fire engulfment, but also that this device is not necessary if its size turns out to be less than that of the aforementioned vent line.

Another design of separator is the vortex separator of Muschelknautz and Mayinger (1986, 1990) described in the CCPS *Guidelines for Vapor Release Mitigation* (1988/4). This separator may be mounted directly above the reactor and may be used to separate the liquid from the vapour prior to the relief device.

17.22.4 Quench systems

The handling of a two-phase mixture in the relief disposal system poses a number of potential problems which have been discussed by Fauske (1986a).

The typical relief train consists of a separator, a scrubber and a flare. A two-phase relief requires a separator, but the typical system has these defects: (1) the relief is liable to be foamy and difficult to separate; (2) the size of the separator is often larger than that of the reactor; (3) the potential may exist for reaction runaway in the separator; and (4) the instantaneous flow may be very high and the flow of scrubbing fluid needs to be correspondingly high.

The method of disposal which Fauske favours to overcome these difficulties is the use of a suitable quench system. This should quench the vapour so that scrubber and/or flare are eliminated, apart from any arrangements needed to deal with small amounts of non-condensables. The selection of the quench fluid is critical, particularly if the reaction mixture has potential for explosive decomposition.

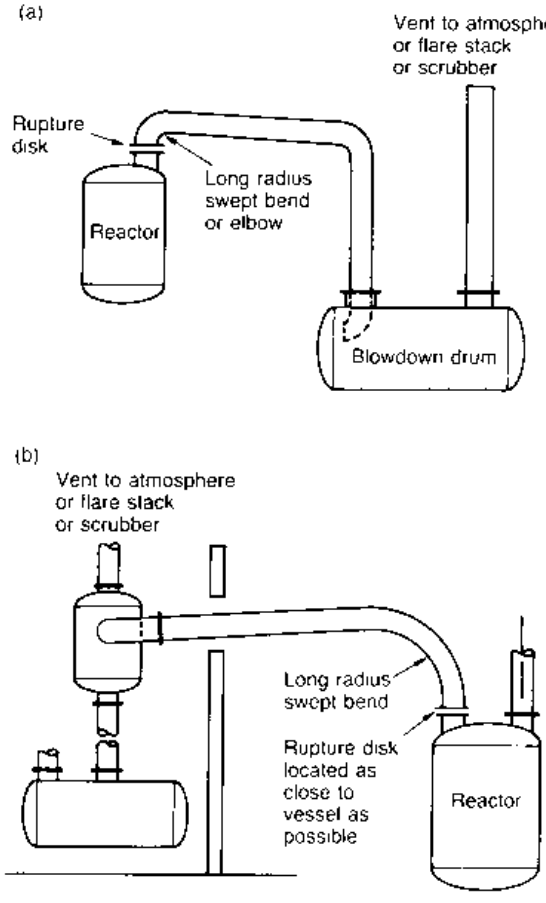


Figure 17.55 *Venting of chemical reactors: blowdown systems (Grossel, 1986): (a) horizontal blowdown drum and (b) knockout drum with separate catchtank (Courtesy of the American Institute of Chemical Engineers)*

17.23 Venting of Reactors: CCPS Work

The CCPS has done work with a view to providing guidance on relief disposal. An outline of draft *Guidelines for Effective Handling of Emergency Release Effluents* has been given by Huff (1992). He describes a methodology for characterizing and handling the relief flow.

The purpose of the guidelines is to provide sufficient information to allow the non-specialist to do the design of the relief disposal system in more than nine cases out of 10 and to be able to identify those which need to be handled by a specialist. Such cases are typically systems which are chemically reactive, contain fractionating multicomponent systems or fluids near their critical point, or involve relief from distributed systems such as long pipe heaters.

The main heads of the guidelines may be summarized as:

(1) relief scenarios;
(2) characterization of flow from protected system;
(3) applicable standards and codes;
(4) relief devices;
(5) flow through relief devices;
(6) installation of relief devices;
(7) disposal scenarios;
(8) disposal strategies;
(9) characterization of flow in relief system.

Guidance is given on the formulation of the relief scenarios and identification of a credible worst case. The problem of scenarios with a high degree of uncertainty is highlighted. Approaches to reducing the relief requirement, such as elimination of aggravating features and the use of alternatives to relief, are described. A checklist is given of events for which relief may be required.

Events in the protected system which may need relief include for non-reactive fluids shut-in pipework and thermal expansion, excess of heating or lack of cooling, and fire exposure, and for reactive fluids runaway reactions.

The characterization of the flow to be handled concentrates particularly on two-phase flow. The mixture vented may be two-phase or it may be superheated so that it becomes two phase in the relief system. During venting, two-phase flow may stop and start. Information is provided on fluid properties, including mixture properties and phase equilibrium.

The terminology and requirements of standards and codes relevant to relief are summarized, both in respect of the relief pressures and the relief devices. The relief devices recognized in the American National Standards Institute (ANSI) system are described. Guidance is given on sizing and on sources of data. Auxiliary components are also described such as block and diverting valves, bleed system components and non-bleed relief monitors.

The guidelines deal with the selection of relief devices, calculation of the flow through relief devices, sizing of the associated pipework, and definition of the flow through the relief disposal system. Methods are given for the calculation of the flow through relief devices, both nozzles and piping, starting with the fundamental equations and following through with working forms of these equations. Devices dealt with include gas safety valves, liquid relief valves, low pressure devices, bursting discs and open vents. Fluids considered include compressible gases and vapours, subcooled liquids, two-phase gas–liquid mixtures and two-phase flashing vapour–liquid mixtures.

The installation of relief devices is treated, including pressure drops in the pipework, provisions to ensure drainage and prevent freezing, static head and siphoning for low pressure devices, and backflow from header connections. Mechanical aspects are also considered, including reaction forces.

Guidance is given on the formulation of the disposal scenarios and identification of a credible worst case, which need not necessarily be the same as the worst case for relief. The potential for vent flows in each phase should be considered and a worst case identified for each phase. The maximum flows and volume to be handled should be determined.

The strategies for relief disposal and the various options are described.

The characterization of the flow in the relief system is considered, including volatility, foaming behaviour, and state of aggregation of phases.

17.24 Venting of Storage Vessels

It is necessary to protect storage vessels against overpressure and this is done by fitting vents. Principal sources of overpressure are operational deviations and fire, but there are numerous other sources, as described in Chapter 20. The fire protection of storage vessels is discussed in Chapter 16.

Fire is not the sole potential source of heat input to a storage vessel. Many chemicals held in storage have the potential to undergo exothermic reaction. Any external heat source, including fire, may act as an initiator. Addition of water may be another. Regard should be had to this effect in considering the venting requirements for storage.

17.24.1 Fire behaviour of atmospheric storage tanks

Work on the fire behaviour and on vent sizing for storage vessels has been described by Fauske, Epstein, Grolmes and Leung (1986) and Fauske (1987a).

Vent sizing for atmospheric storage tanks has traditionally been based on all vapour flow. The aim of the study was to check whether this approach is adequate. The implication of the need to consider two-phase flow would be a large increase in vent size. As a first approximation the increase in vent area required would be of the order of the square root of the ratio of the vapour and liquid densities $(\rho_g/\rho_l)^{\frac{1}{2}}$.

This concern was addressed in an extension of the DIERS project. The work is described in Chapter 15. It was concluded that liquid swell in an externally heated storage tank is essentially limited to the boiling two-phase boundary layer and that for a non-foaming liquid all vapour venting would appear adequate, provided the tank is not completely filled with liquid.

However, for an atmospheric storage tank, it is necessary to avoid entrainment of liquid in the vapour vented. The relation given for the vent area is

$$A = \frac{Q_T}{h_{fg}\rho_g u} \qquad [17.24.1]$$

where A is the area of the vent, h_{fg} is the latent heat of vaporization, Q_T is the total heat input to the tank and u is the velocity of vapour through vent.

The limiting value of the velocity u in Equation 17.24.1 for an atmospheric storage tank is the entrainment velocity u_E:

$$u = u_E \qquad [17.24.2]$$

The relation given for the entrainment velocity is that of Kutateladze (1972):

$$u_E \approx 3.0\left(\frac{\sigma g \rho_l}{\rho_g^2}\right)^{\frac{1}{4}} \qquad [17.24.3]$$

where g is the acceleration due to gravity, ρ_l is the density of the liquid and σ is the surface tension of the liquid.

Fauske (1987a) states that a safety factor of 2 on the vent area determined from Equations 17.24.1–17.24.3 should be adequate even for a foamy liquid.

A criterion for the onset of liquid entrainment in a storage vessel exposed to fire has been given by Epstein, Fauske and Hauser (1989). They consider a hemispherical surface centred on a vent at the centre of the top of a vertical cylindrical vessel. The velocity across this surface is

$$u_s = \frac{1}{2}\left(\frac{a}{s}\right)^2 u_o \qquad [17.24.4]$$

where a is the radius of the vent, s is the radius of the hemisphere, u_s is the velocity across the hemispherical surface and u_o is the velocity up the vent. Onset of entrainment occurs when the velocity u_s attains a critical value u_{scr} at some height $h = s$. Then from Equation 17.24.4

$$h = a\left(\frac{u_o}{2u_{scr}}\right)^{\frac{1}{2}} \qquad [17.24.5]$$

The authors state that this work indicates that rather small freeboard volumes can be tolerated without the occurrence of two-phase venting.

For vessels which can withstand substantially higher pressures, the approach given by Fauske is to take the velocity u in Equation 17.24.1 as

$$u \approx 2\,\Delta P/\rho_g \qquad [17.24.6]$$

where ΔP is the pressure drop through the vent system. He states that a factor of 2 on the vent area determined from Equations 17.24.1 and 17.24.6 is generally consistent with a modest overpressure of some 10–30% above the relief pressure even for a foamy liquid.

Further relationships for the vent area for storage vessels with non-foamy liquid have been given by Fauske, Grolmes and Clare (1989). For an atmospheric storage tank

$$A = \frac{Q_v}{3Fh_{fg}[\sigma g(\rho_l - \rho_g)]^{\frac{1}{4}}\rho_g^{\frac{1}{2}}} \qquad [17.24.7]$$

where F is the flow reduction factor and Q_v is the energy release rate. This equation is based on all vapour flow with no entrained liquid.

For a storage vessel capable of withstanding substantially higher pressure

$$A = \frac{Q_v(R_m T)^{\frac{1}{2}}}{0.62Fh_{fg}P_s} \qquad [17.24.8]$$

where P_s is the absolute set pressure, R_m is the mass basis gas constant and T is the absolute temperature. This equation is based on all vapour critical flow.

Fauske, Grolmes and Clare (1989) describe an approach to vent sizing for storage tanks based on relating the external heating rate to an equivalent self-heat rate and give a graph for checking uninsulated and insulated vessels.

17.24.2 Designs for protection of storage vessels

Fauske (1988b, 1989b) has described a number of designs for the protection of atmospheric storage tanks

and of pressure storage vessels against fire and the hazard of BLEVE.

For atmospheric storage tanks, two designs are given, both involving double wall construction. In one design the intermediate space is filled with water. In the other design there is an air space with facility to inject heating or cooling medium through the space.

For pressure storage vessels, the vessels considered are spheres and there are again two design proposals. The first has an internal spherical baffle so that on fire engulfment the liquid swell would occur in the annulus between the outer wall and the baffle, with liquid being 'pumped' from the bottom to the top of the baffle and then falling down into the centre of the vessel while the vapour is vented. In the other design there is a double wall construction with the vessel held inside a tank, the intermediate space being filled with water.

17.25 Explosive Shock in Air

One of the main effects of an explosion is the creation of a shock wave, or blast wave. This blast wave generates overpressures which may injure people and damage equipment and buildings.

Accounts of explosive shock in air are given in *The Effects of Nuclear Weapons* (Glasstone, 1962) and its later edition (Glasstone and Dolan, 1980), *Explosive Shocks in Air* (Kinney, 1962) and its later edition (Kinney and Graham, 1985), *Explosions in Air* (W.E. Baker, 1973) and *Explosion Hazard and Evaluation* (W.E. Baker *et al.*, 1983).

The situation of prime interest here is that of a chemical explosion at the ground surface and it is this which is mainly considered.

The description given of the explosion is based, unless otherwise stated, on an explosion of high explosive such as TNT.

17.25.1 The blast wave

An explosion in air is accompanied by a very rapid rise in pressure and by the formation of a shock wave. An account of the phenomena involved is given by Glasstone (1962).

The shape of the pressure profile near the centre depends on the type of explosion involved. The initial shape differs for explosions of high explosives, nuclear weapons and flammable vapour clouds.

The initial pressure profile for nuclear explosions is probably the most readily defined. The pressure at the edge of the fireball is approximately twice that at the centre.

With all types of explosion the shock wave travels outwards with the higher pressure parts moving at higher velocities. After it has travelled some distance the shock wave reaches a constant limiting velocity which is greater than the velocity of sound in the air, or in the unburnt gas in the case of a vapour cloud. The shock wave has a profile in which the pressure rises sharply to a peak value and then gradually tails off. As the shock wave travels outwards the peak pressure at the shock front falls.

At some distance from the explosion centre the region of positive pressure, or overpressure, in the shock wave is followed by a region of negative pressure, or underpressure. The underpressure is quite weak and does not exceed about 4 psi.

An idealized representation of the blast wave is given in Figure 17.56. This shows the pressure pulse as a function of distance from the explosion centre with time as the parameter. The shock wave reaches points A–D at times 1–4, respectively, and at these times its pressure profile is as illustrated. The shape of the curve at point A is not shown, since it depends on the type of explosion. As the wave moves outwards, however, the influence of the nature of the explosion declines and the wave establishes a profile which is common to all types of explosion. The curves at points B–D and times 2–4 show the decrease in peak overpressure. The curve at point D and time 4 shows both positive and negative pressures.

The variation of overpressure with time at such a point is illustrated in Figure 17.57. Important parameters are the peak overpressure p^o, the arrival time t_a, the duration time t_d, which is the duration of the positive phase, and the decay parameter α, which defines the shape of the decay curve in the positive phase.

The peak overpressure p^o is more correctly described as the peak side-on overpressure or peak incident overpressure, in order to distinguish it from other peak

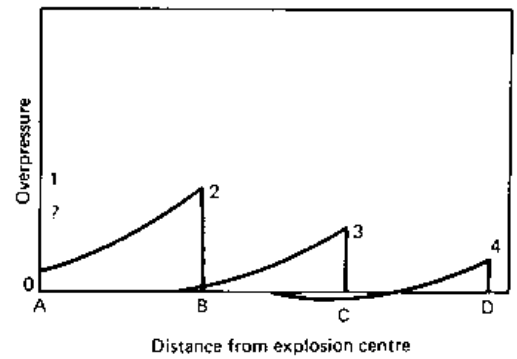


Figure 17.56 *Idealized representation of development of blast wave*

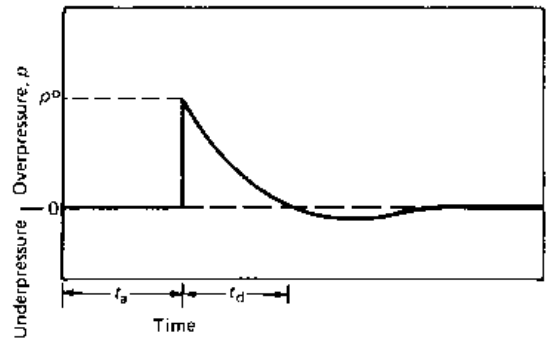


Figure 17.57 *Variation of overpressure from a blast wave with time at a fixed point*

overpressures such as the peak reflected overpressure described below. The peak side-on overpressure is the peak overpressure occurring at the side of a structure being passed by the blast wave.

There are several equations which are used to describe the positive phase of the overpressure decay curve of Figure 17.57. A widely used one is the modified Friedlander equation (Kinney, 1962)

$$p = p^{o}(1 - t/t_{d}\exp(-\alpha t/t_{d}) \quad [17.15.1]$$

where p is overpressure, p^{o} is the peak overpressure, t is the time, t_{d} is the duration time and α is the decay parameter. Another common equation applicable at or below about 10 psi is Equation 17.25.1 with the decay parameter set equal to unity. Information on the decay of overpressure is given by Glasstone (1962, p. 124).

Other important properties of the blast wave, described by Glasstone (1962), are the shock velocity, the particle velocity, or peak wind velocity, behind the shock wave, the peak dynamic pressure and the peak reflected overpressure. The shock velocity is given by

$$U = c_{o}\left(1 + \frac{\gamma + 1}{2\gamma}\frac{p^{o}}{p_{a}}\right)^{\frac{1}{2}} \quad [17.25.2a]$$

where c_{o} is the velocity of sound in air, p_{a} is the absolute ambient pressure (ahead of the shock front), U is the shock velocity and γ is the ratio of specific heats of air. For air $\gamma = 1.4$ and hence

$$U = c_{o}\left(1 + \frac{6}{7}\frac{p^{o}}{p_{a}}\right)^{\frac{1}{2}} \quad [17.25.2b]$$

The particle velocity is given by

$$u = \frac{c_{o}p^{o}}{\gamma p_{a}}\left(1 + \frac{\gamma + 1}{2\gamma}\frac{p^{o}}{p_{a}}\right)^{-\frac{1}{2}} \quad [17.25.3a]$$

where u is the particle velocity. For $\gamma = 1.4$

$$u = \frac{5c_{o}p^{o}}{7p_{a}}\left(1 + \frac{6p^{o}}{7p_{a}}\right)^{-\frac{1}{2}} \quad [17.25.3b]$$

The peak dynamic pressure q^{o} is defined as

$$q^{o} = \frac{1}{2}\rho u^{2} \quad [17.25.4]$$

where q^{o} is the peak dynamic pressure and ρ is the density of air (behind the shock front). This can be shown to be

$$q^{o} = \frac{p^{o2}}{2\gamma p_{a} + (\gamma - 1)p^{o}} \quad [17.25.5a]$$

For $\gamma = 1.4$

$$q^{o} = \frac{5}{2}\frac{p^{o2}}{7p_{a} + p^{o}} \quad [17.25.5b$$

The peak reflected overpressure $p_{r^{o}}$, which occurs if the blast wave strikes a flat surface at normal incidence, is

$$p_{r}^{o} = 2p^{o} + (\gamma + 1)q^{o} \quad [17.25.6a]$$

For $\gamma = 1.4$

$$p_{r}^{o} = 2p^{o} + 2.4q^{o} \quad [17.25.6b]$$

Then substituting for q^{o} from Equation 17.25.5b

$$p_{r}^{o} = 2p^{o}\left(\frac{7p_{a} + 4p^{o}}{7p_{a} + p^{o}}\right) \quad [17.25.7]$$

As stated earlier, the distinction between the peak incident overpressure, or simply the peak overpressure, p^{o} and the peak reflected overpressure p_{r}^{o} is important, and it should always be made clear which overpressure is being referred to.

The peak dynamic pressure is less than the peak overpressure at low values of these two pressures, but greater at higher values. Equation 17.25.5b shows that the cross-over point is about 70 psi (4.83 bar).

The peak reflected overpressure is shown by Equation 17.25.6b to approach a value of twice the peak overpressure for weak shocks in which the peak dynamic pressure is negligible, but to approach a value of eight times the peak overpressure for strong shocks in which the peak dynamic pressure is dominant.

This maximum factor of 8 by which the peak reflected pressure exceeds the peak overpressure is frequently quoted. It depends, however, on the validity of the assumptions underlying Equation 17.25.6b).

17.25.2 Blast scaling

The characteristics of the blast wave produced by an explosion are generally determined by the application of the scaling laws.

As described in Section 17.3 in relation to explosives, there are a number of scaling laws which relate explosion effects such as overpressure, damage circle radius, crater radius and sympathetic detonation distance.

For the blast wave from an explosion the scaling relation which is much the most widely used is the 'cube root' law, which was first enunciated by Hopkinson (1915). This law states that when two charges of the same explosive and geometry but of different size are detonated in the same atmosphere, self-similar shock waves are produced at the same scaled distances. The scaled distance is defined as

$$z = \frac{r}{W^{\frac{1}{3}}} \quad [17.25.8]$$

where r is the distance, W is the mass of explosive and z is the scaled distance. It should be noted that the scaled distance is not dimensionless.

Strictly the relevant scaling variable is the energy E rather than the mass of explosive W, but for a particular explosive it is usual to assume that the energy released is proportional to the mass of explosive.

The cube root index in the scaling law is related to the fact that energy is deposited into a spherical, or hemispherical, region, the volume of which varies with the cube of the radius.

Other scaling laws are described by W.E. Baker (1973).

Another parameter which may be used in blast scaling is the yield factor λ, which is defined as

$$\lambda = \left(\frac{W}{W_{o}}\right)^{\frac{1}{3}} \quad [17.25.9]$$

where λ is the yield factor, and the subscript o denotes the reference value.

Since from Equation 17.25.8 self-similar shock effects occur at the same scaled distance

$$z = \frac{r_o}{W_o^{\frac{1}{3}}} = \frac{r}{W^{\frac{1}{3}}} \quad [17.25.10]$$

or, introducing the yield factor from Equation 17.25.9),

$$r = \lambda r_o \quad [17.25.11]$$

where r_o is the reference distance.

If in Equation 17.25.9, $W_o = 1$, then 1 is numerically equal to $W^{\frac{1}{3}}$, and Equation 17.25.11 reduces to Equation 17.25.8 with r_o numerically equal to z.

The application of the scaling laws to the principal blast parameters is now considered.

17.25.3 Peak overpressure

An important parameter of the blast wave is the peak side-on overpressure p^o. The scaling relation for this parameter is

$$p^o = f(z) \quad [17.25.12]$$

Equation 17.25.12 states that a given peak overpressure occurs at a given scaled distance.

This scaling law implies, for example, that for a given peak overpressure an increase in the mass of explosive by a factor of 1000 corresponds to an increase in the distance from the explosion by a factor of 10.

The decay of the peak overpressure is given by Equation 17.25.1).

The peak overpressure is frequently presented in the form of the ratio

$$p_s = \frac{p^o}{p_a} \quad [17.25.13]$$

where p_a is the ambient pressure and p_s is the scaled pressure.

17.25.4 Arrival and duration time

Blast scaling applies to the time parameters arrival time and duration time. The scaled time τ is defined as

$$\tau = \frac{t}{W^{\frac{1}{3}}} \quad [17.25.14]$$

where t is the time and τ is the scaled time. It should be noted that scaled time is not dimensionless. Then from Equation 17.25.14

$$\tau = \frac{t_o}{W_o^{\frac{1}{3}}} \quad [17.25.15]$$

where t_o is a reference time. The scaled arrival time and the scaled duration time are thus

$$\tau_a = \frac{t_a}{W^{\frac{1}{3}}} \quad [17.25.16]$$

and

$$\tau_d = \frac{t_d}{W^{\frac{1}{3}}} \quad [17.25.17]$$

where t_a is the arrival time, τ_a is the scaled arrival time and τ_d the scaled duration time.

In terms of the yield factor λ

$$t = \lambda t_o \quad [17.25.18]$$

where t_o is a reference time.

17.25.5 Dynamic pressure

Another important parameter of the blast is the peak dynamic pressure q^o. This is defined by Equation 17.25.4) and may be obtained from Equation 17.25.5).

Information on the decay of the dynamic pressure is given by Glasstone (1962).

17.25.6 Overpressure impulse

Further important parameters of the blast are the overpressure and dynamic impulses. The positive phase overpressure impulse, overpressure impulse, or simply impulse, i_p is the integral of the overpressure during the positive phase:

$$i_p = \int_0^{t_d} p \, dt \quad [17.25.19]$$

Substituting Equation 17.25.1) in Equation 17.25.19 gives

$$i_p = p^o t_d \left(\frac{1}{\alpha} - \frac{1}{\alpha^2} [1 - \exp(-\alpha)] \right) \quad [17.25.20]$$

The simplifying assumption is sometimes made that the impulse takes the form of a triangle. In this case it may be approximated by

$$i_p \approx \frac{1}{2} p^o t_d \quad [17.25.21]$$

The overpressure impulse i_p is another parameter of the blast wave to which scaling is applied. The scaled impulse i_s is defined as

$$i_s = \frac{i_p}{W^{\frac{1}{3}}} \quad [17.25.22]$$

17.25.7 Dynamic pressure impulse

The dynamic pressure impulse i_q is

$$i_q = \int_0^{t_d} q \, dt \quad [17.25.23]$$

As for the overpressure impulse, it is often assumed that the dynamic pressure impulse takes the form of a triangle so that it may be approximated by

$$i_q \approx \frac{1}{2} q^o t_q \quad [17.25.24]$$

Information on the impulse and duration time for the dynamic pressure is not as readily available as for the corresponding parameters for overpressure. The following empirical relation is given for the dynamic pressure impulse by Richmond and Fletcher (1971):

$$\ln R = \frac{5.4054 + 1.1067 \ln W - \ln i_q}{2.3201} \quad [17.25.25]$$

where i_q is the dynamic pressure impulse (psi ms), R is the distance (ft) and W the mass of explosive (lb) (as TNT equivalent).

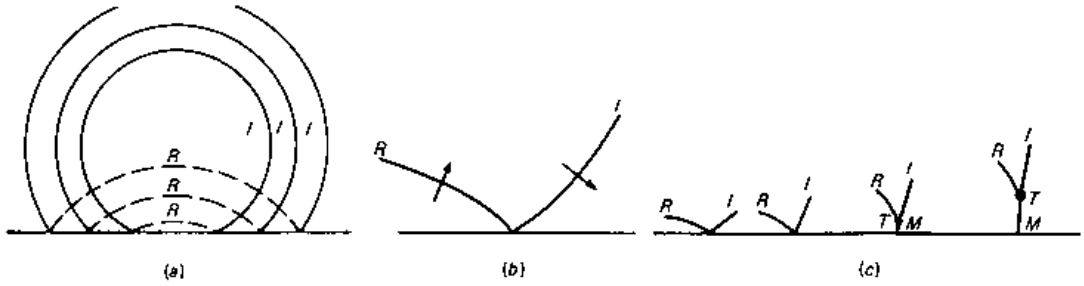


Figure 17.58 *Blast waves produced by an air burst: (a) development of blast wave; (b) incident and reflected waves; (c) development of Mach stem. I, incident wave; R, reflected wave; M, Mach stem; T, triple point*

17.25.8 Air bursts

So far the account given of the blast wave is a general one, and no distinction has been made between a burst occurring in free air and one occurring on the ground surface.

If the explosion is an air burst, or an explosion which occurs at some height above ground level, the behaviour of the shock waves on reaching the ground surface is rather more complex. The situation may be explained by reference to Figure 17.58. As shown in Figures 17.58(a) and 17.58(b), the incident shock I strikes the ground and gives rise to a reflected shock wave *R*. The reflected shock wave passes through an atmosphere which has already been heated and compressed by the incident wave. It therefore travels faster and tends to overtake the incident wave. Where this happens, the two waves fuse at the triple point *T* and form a Mach system *M* below this point, as shown in Figure 17.58(c). The Mach stem is a shock front similar to that generated by ground level explosions.

For moderate heights the Mach stems forms at a distance from the ground which is approximately equal to the height of the explosion (Glasstone, 1962, Figure 3.67a).

17.26 Condensed Phase Explosions

An explosion of a high explosive is referred to as a condensed phase explosion. The explosive which serves as the reference standard is TNT.

In this section consideration is given primarily to the characteristics of the explosion itself. The effects of the explosion are considered in detail later. However, an account is first given of some incidents involving high explosives.

17.26.1 Condensed phase explosion incidents

Condensed phase explosions include explosions of munitions, commercial explosives and ammonium nitrate.

An account of early condensed phase explosions is given in *History of Explosions* (Assheton, 1930). Some further incidents are detailed in *Darkest Hours* (J.R. Nash, 1976) and *Handbuch Störfalle* (Kier and Müller, 1983). Apart from this, information has to be sought mainly in the accounts of individual explosions. Incident data are also available from the Explosions Incidents Data Service (EIDAS) data bank of the Safety and Reliability Directorate (SRD).

Appendix 1 includes a section devoted to condensed phase explosions. Some principal explosions are given in Table 17.24, with incidents involving munitions and commercial explosives listed in Section A and those involving ammonium nitrate in Section B. Further information on these incidents is given in Table A1.2 in Appendix 1. The criteria for inclusion of condensed phase explosion incidents in both these tables is that the incident is a major one, that it is of technical interest and/or that it is frequently referenced. The tables give only a small sample of the condensed phase explosions which have occurred.

In the early years of the chemical industry, many of the worst incidents involved condensed phase explosives, including ammonium nitrate.

Incidents involving munitions and commercial explosives include the explosion of the munition ship *Mont Blanc* in the harbour at Halifax, Nova Scotia, in 1917 in which 1963 people were killed (Case History A3). Within a radius of about three quarters of a mile, destruction was almost complete. It was estimated that 95% of the glass in the city was broken.

Also in 1917 there was an explosion at a munitions works in Silvertown, London, and another, less well known, explosion at a chemical works at Ashton, Manchester (Case Histories A4 and A2, respectively).

In 1989 there was an explosion of a load of commercial explosives on a road vehicle at Peterborough in the UK (Case History A125). This incident has significance for the transport of explosives.

Turning to ammonium nitrate, the explosion at Oppau in 1921 resulted from the use of blasting powder to break up stored piles of the material (Case History A5). It created a crater 250 ft in diameter and 50 ft deep, destroyed hundreds of houses and killed 561 people.

The explosions at Texas City in 1947 occurred in two ships, the *Grandcamp* and the *High Flyer*, both of which were carrying ammonium nitrate (Case History A16). They damaged thousands of buildings, hurled missiles several miles and killed 552 people. The fires burned for nearly a week.

Table 17.24 *Some condensed phase explosion incidents*

A Munitions and commercial explosives

Date	*Location*	*Explosive*[a]	Plant/transport	Deaths/injuries
1913	Mexico City	Dynamite	Road vehicle	41+, ≈100i
1917	Ashton, UK			
	Halifax, Nova Scotia	Munitions	Ship	1963d, ≈8000i
	Silvertown, UK	TNT	Munitions works	69d, 426i
1944	Fauld, UK	Munitions	Munitions store	68d, 22i
1956	Cali, Columbia	Munitions, dynamite	Seven road vehicles	≈1200d
1971	Waco, GA	Explosives	Road vehicle	5d, 33i
1985	Checotah, OK	Munitions	Road vehicle	0d, 49i
1989	Peterborough, UK	Explosives	Road vehicle	1d, 107i
1990	Meerut, India	Explosives	Road vehicle	50d
1991	Thung Maproah, Thailand	Dynamite	Road vehicle	123d

B Ammonium nitrate

Date	*Location*	*Plant/transport*	*Deaths/injuries*
1918	Morgan, NJ		64d
1921	Oppau, Germany	Chemical works	561d
1942	Tessenderloo, Belgium		>100d
1944	Bombay Docks, India	Ship	>350d, 1800i
1947	Brest, France	Ship	21d
1947	Texas City, TX	Two ships	552d, ≈3000i

[a] Only the main item of the load is given. In some cases there were other items such as detonators, boosters, etc.

17.26.2 TNT explosion model

The blast characteristics of a TNT explosion are important in their own right and are also sometimes used in modelling other types of explosion. There is available much more information on explosions of explosives, particularly TNT, than for other cases.

Sources of information on the blast characteristics from the explosion of TNT charges include *Structural Defence* (Christopherson, 1946), *The Effects of Nuclear Weapons* (Glasstone, 1962; Glasstone and Dolan, 1980), *Explosive Shock in Air* (Kinney, 1962; Kinney and Graham, 1985), *Hazards of Chemical Rockets and Propellants Handbook* (Jensen, 1972), *Explosions in Air* (W.E. Baker, 1973) and *Explosion Hazard and Evaluation* (W.E. Baker *et al.*, 1983) and work by Hoffman and Mills (1956), Goodman (1960), Kingery and Pannill (1964), Kingery (1966), Swisdak (1975) and Kingery and Bulmash (1984).

In principle, the blast characteristics of a TNT explosion depend on the mass and shape of the charge and also on the point(s) of ignition.

For a TNT explosion the two standard types of reference data are those for explosions from a point source and from a spherical charge. The blast parameters for the two explosions are slightly different. For overpressure, for example, the initial effect of a finite charge size is to reduce the overpressure very close to the charge relative to that from a point source. This effect holds for a distance of some five charge diameters. At greater distances, however, the overpressure from a spherical charge is greater, being approximately equivalent to that from a point source with one-third greater energy release.

Other features which affect the blast characteristics include the location relative to sea level and the meteorological conditions.

Before proceeding further, it is necessary to draw attention to the fact that there is a degree of scatter in the experimental results for condensed phase explosions, including TNT explosions. W.E. Baker *et al.* (1983, Figure 2–3) give for high explosives a plot of peak overpressure vs scaled distance for which the highest and lowest curves of peak overpressure differ in parts by almost an order of magnitude. The most recent data on the plot was from W.E. Baker (1973). On the other hand, work on the measurement of peak overpressure from TNT explosions has continued, and it is to be expected that the more recent results are more accurate.

The two reference standards for data on a TNT explosion are a free air burst (where the blast wave is not affected by interaction with the ground), which has spherical symmetry, and a surface burst, which has hemispherical symmetry.

The principal parameters of the blast wave from a TNT explosion are the peak side-on overpressure p^o, the impulse of the positive phase i, the duration of the positive phase t_d and the arrival time t_a. Values of these parameters may be presented in scaled or unscaled form. The scaled forms are those given in Equations 17.25.13, 17.25.22, 17.25.17 and 17.25.16), respectively. Thus the

unscaled and scaled forms of the parameters in SI units are:

	Unscaled	*Scaled*
Peak overpressure	p^o (Pa)	$p_s = p^o/p_a$ (–)
Impulse	i_p (Pa s)	$i_s = i_p/W^{\frac{1}{3}}$ (Pa s/kg$^{\frac{1}{3}}$)
Duration time	t_d (s)	$\tau_d = t_d/W^{\frac{1}{3}}$ (s/kg$^{\frac{1}{3}}$)
Arrival time	t_a (s)	$\tau_a = t_a/W^{\frac{1}{3}}$ (s/kg$^{\frac{1}{3}}$)

where p_a is atmospheric pressure (Pa) and W is the mass of explosive (kg).

Values for TNT explosion parameters which appear to have gained general acceptance are those determined at the Ballistics Research Laboratory, Aberdeen Proving Ground, Maryland, by Kingery and co-workers (Kingery and Pannill, 1964; Kingery, 1966). A review of the data from this and other work has been made by Kingery and Bulmash (1984), who give data and correlations both for free air bursts and surface bursts.

Figure 17.59(a) is a plot of the four parameters mentioned for a free air burst (spherical symmetry) based on the data of Kingery and Bulmash. The graph is plotted in terms of the scaled parameters p_s, i_s, τ_d and τ_a. Figure 17.59(b) is the corresponding plot for a surface burst (hemispherical symmetry), again from Kingery and Bulmash.

Other widely used values for TNT explosions are those of and those of W.E. Baker *et al.* (1983) and of Kinney and Graham (1985). Baker *et al.* give a graph (their Figure 2.45) for free air bursts which is broadly similar to Figure 17.59(a), but which also includes several other parameters. Kinney and Graham give a graph for peak overpressure and data in tabular form for all four parameters treated here.

Work quoted by Kingery and Bulmash includes that of Goodman (1960), Kingery (1966), W.E. Baker (1973), Swisdak (1975) and Reisler, Pettit and Kennedy (1976, 1977), and that quoted by Kinney and Graham includes that of Hoffman and Mills (1956), Goodman (1960), Keefer *et al.* (1966) and Kingery (1966).

Table 17.25 shows a comparison of the values for free air bursts by Kingery and Bulmash with those of Kinney and Graham.

As an illustration of the use of the Figure 17.59, consider the determination from Figure 17.59(a) for a free air burst of the values of the peak overpressure p^o and the impulse i_p for a charge weight W of 8 kg at a distance of 10 m with ambient pressure 1.01×10^5 Pa. Then

$$z = 10/8^{\frac{1}{3}}$$

$$= 5\ m/kg^{\frac{1}{3}}$$

$$p_s = 0.31$$

$$p^o = p_s \times p_a$$

$$= 0.31 \times 1.01 \times 10^5$$

$$= 0.313 \times 10^5 \text{ Pa}$$

$$i_s = 4.1 \times 10^{-4} \text{ Pa s kg}^{\frac{1}{3}}$$

$$i_p = i_s \times W^{\frac{1}{3}}$$

$$= 4.1 \times 10^{-4} \times 8^{\frac{1}{3}}$$

$$= 8.2 \times 10^{-4} \text{ Pa s}$$

The original graphs given by Kingery and Bulmash are plots showing the unscaled parameters p^o, i_p, t_d and t_a for an explosion involving 1 kg of TNT ($W = 1$). The graphs given in Figure 17.59 are the same plots but with the parameters shown as scaled.

Also shown on the full curve in Figure 17.59(a) are the effects on the peak overpressure in the far field of surface temperature inversion and unstable atmosphere. Under surface temperature inversion conditions there can be a two- or three-fold increase in peak overpressure.

The variation of the blast parameters may also be expressed in the form of equations. Kingery and Bulmash use for the peak overpressure p^o, impulse i_p, duration time t_d and arrival time t_s of a 1 kg explosion of TNT correlations of the following form. For a given parameter ϕ the relations are

$$U = a + b \log_{10} z \qquad [17.26.1]$$

$$\log_{10} \phi = \sum_{i=0}^{n} c_i U^i \qquad [17.26.2]$$

The values of the constants in these equations given by these authors are shown in Table 17.26. In these

Table 17.25 *Some values*[a] *of the side-on blast parameters for a free air explosion of TNT*

Scaled distance, z $z(m/kg^{\frac{1}{3}})$	*Peak overpressure,* p^o (Pa)		*Impulse,* i_p (Pa s)		*Duration time,* t_d (s)	
	K&B	K&G	K&B	K&G	K&B	K&G
0.5	38.8×10^5	39.0×10^5	1.41×10^2	1.07×10^2	3.20×10^{-4}	0.84×10^{-4}
1.0	9.35×10^5	9.83×10^5	1.75×10^2	1.02×10^2	1.79×10^{-3}	0.52×10^{-3}
5	0.313×10^5	0.285×10^5	4.06×10^1	3×10^1	3.33×10^{-3}	2.47×10^{-3}
10	0.111×10^5	0.097×10^5	2.11×10^1	1.51×10^1	4.20×10^{-3}	3.47×10^{-3}
40	0.017×10^5	0.021×10^5	5.30	4.0	6.16×10^{-3}	4.15×10^{-3}

[a] K&B, Kingery and Bulmash (1985); K&G, Kinney and Graham (1985).

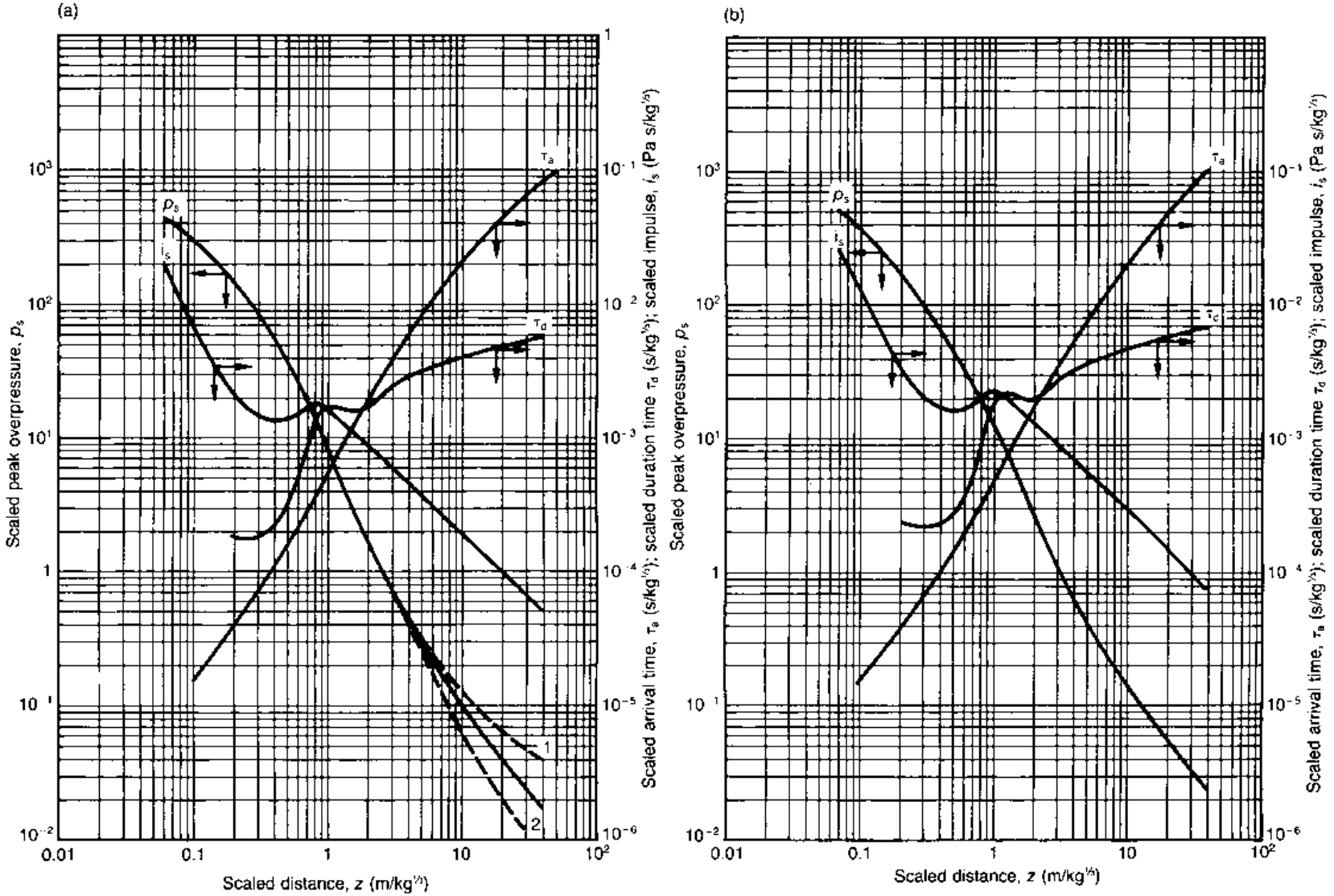


Figure 17.59 *Some side-on blast parameters for a TNT explosion (after Kingery and Bulmash, 1985): (a) free air burst (spherical symmetry) and (b) surface burst (hemispherical symmetry)*

Table 17.26 *Constants in correlations of side-on blast parameters for an explosion of TNT of Kingery and Bulmash*

A Free air burst

Range	*Constant*	*Parameter*			
		p^o (kPa)	i_p (kPa ms)	t_d (ms)	t_a (ms)
1		$0.0531 \leq z \leq 40$	$0.0531 \leq z \leq 0.792$	$0.147 \leq z \leq 0.888$	$0.0531 \leq z \leq 40$
2		–	$0.792 \leq z \leq 40$	$0.888 \leq z \leq 2.28$	–
3		–	–	$2.28 \leq z \leq 40$	–
1	a	−0.214 362 789 151	2.347 239 213 54	2.263 672 684 96	−0.253 273 111 999
2		–	−1.753 056 603 15	−1.333 612 067 14	–
3		–	–	−3.130 058 053 46	–
1	b	1.350 342 499 93	3.242 990 664 75	5.115 885 543 05	1.374 070 437 77
2		–	2.306 292 318 03	9.299 628 861 1	–
3		–	–	3.152 472 536 4	–
1	c_o	2.611 368 669	2.388 305 167 57	−0.686 608 550 419	0.072 070 778 763 7
2		–	1.551 972 271 15	0.230 318 410 78	–
3		–	–	0.621 036 276 475	–
1	c_1	−1.690 128 013 9	−0.443 749 377 691	0.164 953 518 069	1.364 568 712 14
2		–	−0.404 632 920 88	−0.029 794 426 896 9	–
3		–	–	0.096 703 199 555 2	–
1	c_2	0.008 049 735 919 51	0.168 825 414 684	0.127 788 499 497	−0.057 003 569 278 4
2		–	−0.014 272 194 608 2	0.030 632 954 294 1	–
3		–	–	−0.008 013 020 596 67	–
1	c_3	0.336 743 114 941	0.034 813 803 030 8	0.002 91 430 135 946	−0.182 832 224 796
2		–	0.009 123 663 166 17	0.018 340 557 407 4	–
3		–	–	0.004 827 057 797 32	–
1	c_4	−0.005 162 263 513 34	−0.010 435 192 824	0.001 879 574 492 27	0.011 885 143 601 4
2		–	−0.000 675 068 140 4	−0.017 396 466 628 6	–
3		–	–	0.001 875 872 722 87	–
1	c_5	−0.080 922 861 988 8	–	0.017 341 396 254 3	0.043 264 868 762 7
2		–	−0.008 008 637 189 01	−0.001 063 219 635 76	–
3		–	–	−0.002 467 385 093 21	–
1	c_6	−0.004 785 072 667 47	–	0.002 697 397 580 43	−0.000 799 736 783 4
2		–	0.003 148 195 159 31	0.005 620 600 312 8	–
3		–	–	−0.000 841 116 668	–
1	c_7	0.007 930 304 722 42	–	−0.003 619 765 027 98	−0.004 360 735 550 33
2		–	0.001 520 447 833 82	0.000 161 821 749 9	–
3		–	–	0.000 619 329 105 2	–
1	c_8	0.000 768 446 973 5	–	−0.001 009 265 779 34	–
2		–	−0.000 747 026 589 9	−0.000 686 018 894 4	–
3		–	–	–	–

B Surface burst

Range	*Constant*	*Parameter*			
		p^o (kPa)	i_p (kPa ms)	t_d (ms)	t_a (ms)
1		$0.0674 \leq z \leq 40$	$0.0674 \leq z \leq 0.955$	$0.178 \leq z \leq 1.01$	$0.0674 \leq z \leq 40$
2		–	$0.955 \leq z \leq 40$	$1.01 \leq z \leq 2.78$	–
3		–	–	$2.78 \leq z \leq 40$	–
1	a	−0.214 362 789 151	2.067 619 087 21	1.929 461 540 68	−0.202 425 716 178
2		–	−1.947 088 467 47	−2.124 925 252 16	–
3		–	–	−3.536 262 180 91	–
1	b	1.350 342 499 93	3.076 032 966 6	5.250 991 939 25	1.377 842 236 35
2		–	2.406 977 454 06	9.299 628 861 1	–
3		–	–	3.463 497 455 71	–
1	c_o	2.780 769 165 77	2.524 556 209 25	−0.614 227 603 559	−0.059 163 428 804 6
2		–	1.672 816 458 63	0.315 409 245 784	–
3		–	–	0.686 906 642 409	–
1	c_1	−1.695 898 874 1	−0.502 992 763 686	0.130 143 717 675	1.357 064 962 58
2		–	−0.384 519 026 965	−0.029 794 426 897 6	–
3		–	–	0.093 303 530 400 9	–
1	c_2	−0.154 159 376 846	0.171 335 645 235	0.134 872 511 954	0.052 492 798 645
2		–	−0.026 081 670 630 1	0.030 632 954 288	–
3		–	–	−0.000 584 942 088 3	–
1	c_3	0.514 060 730 593	0.045 017 696 305 1	0.039 157 427 690 6	−0.196 563 954 086
2		–	0.005 957 987 538 22	0.018 340 557 408 6	–
3		–	–	−0.002 268 849 950 13	–
1	c_4	0.098 853 436 527 4	−0.011 896 462 640 2	−0.004 759 336 647 02	−0.060 177 005 228 8
2		–	0.014 544 526 107	−0.017 396 466 621 1	–
3		–	–	−0.002 959 085 915 05	–
1	c_5	−0.293 912 623 038	–	−0.004 281 445 980 08	0.069 636 027 089 1
2		–	−0.006 632 893 347 34	−0.001 063 219 636 33	–
3		–	–	0.001 480 298 689 29	–
1	c_6	−0.026 811 234 501 9	–	–	0.021 529 749 009 2
2		–	−0.002 841 893 272 04	0.005 620 600 309 77	–
3		–	–	–	–
1	c_7	0.109 097 496 421	–	–	−0.016 165 893 078 5
2		–	0.001 364 481 622 7	0.000 161 821 749 9	–
3		–	–	–	–
1	c_8	0.001 628 467 563 11	–	–	−0.002 325 319 702 94
2		–	–	−0.000 686 018 894 4	–
3		–	–	–	–
1	c_9	−0.021 463 103 024 2	–	–	0.001 477 520 675 24
2		–	–	–	–
3		–	–	–	–
1	c_{10}	0.000 145 672 338 2	–	–	–
2		–	–	–	–
3		–	–	–	–
1	c_{11}	0.001 678 477 522 66	–	–	–
2		–	–	–	–
3		–	–	–	–

equations the units of the parameters are as shown in the table.

Kinney and Graham have given their values of the peak overpressure, impulse and duration time from an explosion of 1 kg of TNT in the form of network equations. In SI units for the scaled peak overpressure p_s

$$p_s = \frac{808[1 + (z/4.50)^2]}{[1 + (z/0.048)^2]^{\frac{1}{2}}[1 + (z/0.32)^2]^{\frac{1}{2}}[1 + (z/1.35)^2]^{\frac{1}{2}}} \quad [17.26.3]$$

for the impulse

$$i_p = \frac{0.067[1 + (z/0.23)^4]^{\frac{1}{2}}}{z^2[1 + (z/1.55)^3]^{\frac{1}{2}}} \quad [17.26.4]$$

and for the scaled duration time

$$\frac{t_d}{W^{\frac{1}{3}}} = \frac{980[1 + (z/0.54)^{10}]}{[1 + (z/0.02)^3][1 + (z/0.74)^6][1 + (z/6.9)^2]^{\frac{1}{2}}} \quad [17.26.5]$$

where p_s is the scaled peak overpressure, i_p is the impulse (bar ms), t_d is the duration time (ms), W is the mass of explosive (kg) and z is the scaled distance (m/kg$^{\frac{1}{3}}$).

It has already been mentioned that the blast parameters for a surface burst (hemispherical symmetry) can be obtained from those for a free air burst (spherical symmetry) by using in the relations for the latter a charge weight suitably modified to account for the concentration of energy into the hemisphere rather than the sphere. The presumption is that this yield ratio, or symmetry factor, should be 2, and it is this value which is commonly used.

Table 17.27 gives a comparison between values of the peak overpressure, impulse and duration time for a surface burst calculated directly from the surface burst model and values calculated from the free air burst model using a yield ratio of 2, based on the Kingery and Bulmash data for these two cases. Thus in using the free air burst model, the modified charge weight used is $2W$, which introduces a correction factor of $2^{\frac{1}{3}}$ (=1.26). The scaled distance to be used for the free air burst case is therefore that for the surface burst case divided by 1.26. The scaled parameters are then obtained. No further correction is required for the peak overpressure, which is scaled not by charge weight but by ambient pressure, but for the two parameters for which charge weight (or rather its cube root) are the scaling factor, the impulse and the duration time, the scaled values are multiplied by 1.26 to convert them to the unscaled values.

17.26.3 TNT explosion model: methods of Baker *et al.*

Work on the correlation of blast parameters which is frequently utilized is that of W.E. Baker *et al.* (1983). Some discussion of their treatment is therefore necessary.

At different points in their account these authors use two slightly different methods of correlation. They may be distinguished by reference to the scaled distance used. In the first method this is expressed as

$$z = \frac{R}{W^{\frac{1}{3}}} \quad [17.26.6]$$

where R is the distance (m), W is the mass of explosive (kg) and z is the scaled distance (m/kg$^{\frac{1}{3}}$).

Using this scaled distance the authors present for TNT graphs for (1) side-on blast parameters, (2) normally reflected blast parameters and (3) additional side-on blast parameters (their Figures 2–45 to 2–47, respectively). These graphs cover a large number of blast parameters and wide range of scaled distance.

In the second method used by these authors, described earlier in W.E. Baker *et al.* (1975), the scaled distance is expressed as

$$\bar{R} = r\left(\frac{p_o}{E_{ex}}\right)^{\frac{1}{3}} \quad [17.26.7]$$

where E_{ex} is the explosion energy (J), p_o is the absolute pressure of the ambient air (Pa), r is the distance (m) and $\bar{R}$ is the scaled distance.

The scaled overpressure is defined as

$$\bar{P}_s = \frac{p_s}{p_o} - 1 \quad [17.26.8]$$

where p_s is the absolute peak side-on pressure (Pa) and $\bar{P}_s$ is the scaled peak side-on overpressure.

The scaled impulse is defined as

$$\bar{I} = \frac{i_s a_o}{p_o^{\frac{2}{3}} E_{ex}^{\frac{1}{3}}} \quad [17.26.9]$$

where a_o is the speed of sound in the gas (m/s), i_s is the side-on impulse (Pa s) and $\bar{I}$ is the scaled side-on impulse.

Figures 17.60 and 17.61 show the curves for scaled peak side-on overpressure and scaled impulse given by W.E. Baker *et al.* (1975) for pentolite.

Table 17.27 *Comparison of the side-on blast parameters for a surface explosion calculated (a) from a surface explosion relation and (b) from a free air explosion relation*

Scaled distance,	*Hemispherical model*			*Scaled distance,*	*Spherical model using yield factor of 2*		
z (m/kg$^{\frac{1}{3}}$)	p^o (Pa)	i_p (Pa s)	t_d (s)	z (m/kg$^{\frac{1}{3}}$)	p^o (Pa)	i_p (Pa s)	t_d (s)
0.5	48.7×10^5	1.66×10^2	2.81×10^{-4}	0.4	57.4×10^5	1.73×10^2	2.87×10^{-4}
2.5	1.72×10^5	1.09×10^2	2.36×10^{-3}	2	1.95×10^5	1.16×10^2	2.33×10^{-3}
5	0.432×10^5	5.93×10^1	3.79×10^{-3}	4	0.465×10^5	6.27×10^1	3.86×10^{-3}

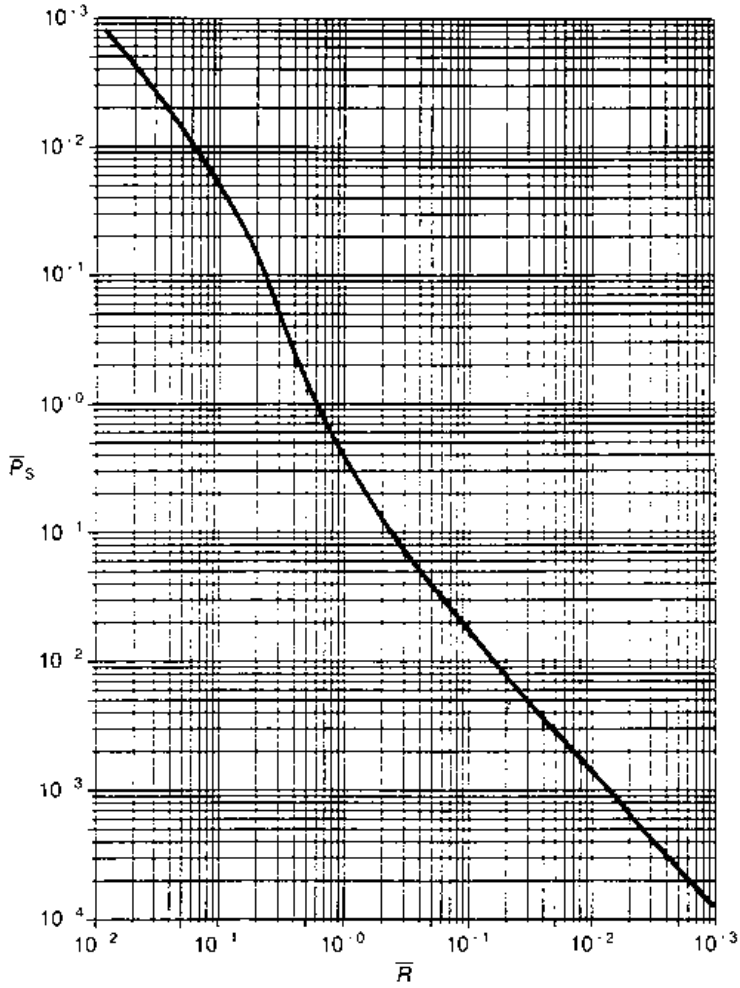


Figure 17.60 *Scaled peak side-on overpressure for a pentolite explosion (W.E. Baker et al., 1975)*

The actual peak side-on overpressure $\bar{P}_s$ and side-on impulse $\bar{T}$ are then obtained from Equations 17.27.8 and 17.27.9.

This second method, utilizing Equations 17.27.7)–17.27.9, is also that used by Baker and co-workers for the treatment of vessel burst explosions and vapour cloud explosions, as described in Sections 17.27 and 17.28, respectively.

17.26.4 TNT equivalent model

In the absence of models for other types of explosion, such as vessel burst or vapour cloud explosion, it has frequently been the practice to model such explosions by estimating the energy of the explosion, calculating the TNT equivalent and then treating the explosion as if it were one from a TNT charge. In other words, use has been made of a TNT equivalent model.

For example, the TNT equivalent model was used by Brasie and Simpson (1968) in an investigation of vapour cloud explosions.

However, the characteristics of the blast from the explosion of a TNT charge are significantly different from those given by other explosions. The pressure developed by a TNT explosion confined within the boundaries of the charge is of the order of half a million bar, which is very much higher than that within a bursting vessel or vapour cloud.

Comparing the profile of the peak overpressure from a TNT explosion with that from a vapour cloud explosion, in the near field the peak overpressure of the TNT explosion is higher, in the far field it is less. One consequence of this is that the use of the TNT equivalent model is not conservative in the far field.

The duration time of a TNT explosion is relatively short. This contrasts with a vapour cloud explosion, for which the duration time, and hence the impulse, is

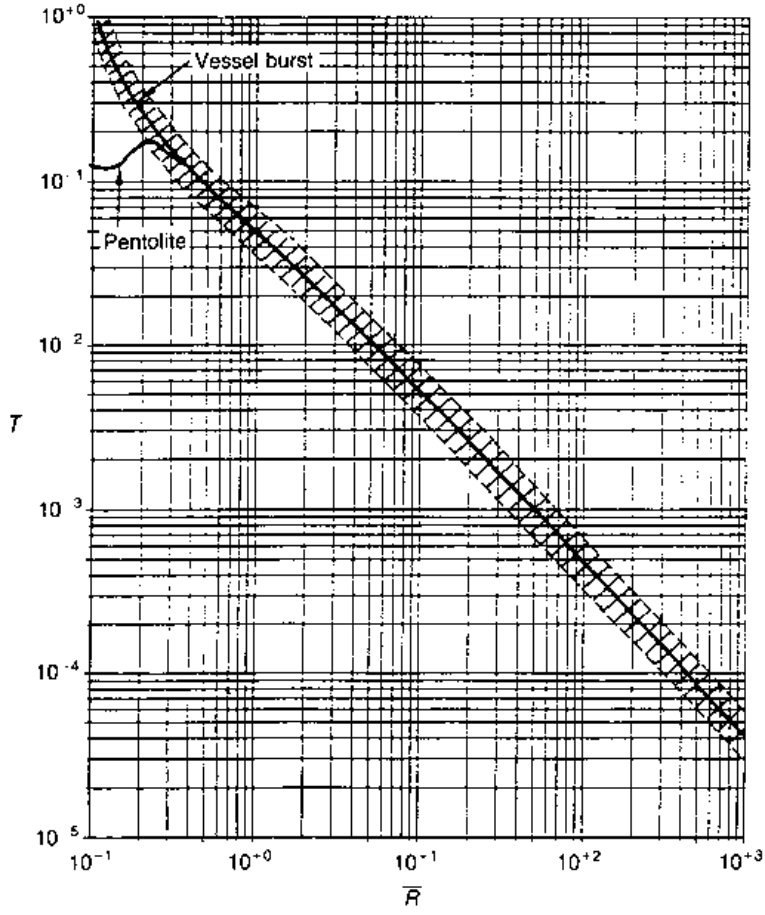


Figure 17.61 *Scaled side-on impulse for a pentolite explosion (W.E. Baker et al., 1975)*

longer. This is another feature which is not conservative in the use of the TNT equivalent model.

A further discussion of the application of the TNT equivalent model to vapour cloud explosions is given in Section 17.28.

17.27 Vessel Burst Explosions

Turning now to types of explosion more typical of process plant, consideration is given first to vessel bursts in which the energy of explosion derives from the pressure in the vessel and the explosion is essentially physical rather than chemical.

17.27.1 Experimental studies

Only a small amount of experimental work on the bursting of gas-filled vessels is reported in the literature.

Boyer *et al.* (1958) performed tests on the bursting of small gas-filled glass spheres. Another set of small-scale experiments using such apparatus is that of Esparza and Baker (1977). In this latter work the spheres ranged up to 102 mm diameter and the burst pressures up to 5.25 MPa.

Experiments with metal containers were conducted by Pittman (1972a,b), using volumes up to 0.17 m^3. The burst pressures were about 4 MPa for cylindrical vessels and 55 MPa for spherical ones. Subsequently Pittman (1976) carried out tests on 0.28 m^3 metal spheres with burst pressures up to 100–345 MPa.

17.27.2 Empirical features

This work brings out several relevant empirical features.

The work of Pittman (1972a,b), which involved high pressures, demonstrates the need to take into account in estimating the energy of explosion for such cases the non-ideal behaviour of the gas.

The differences between the behaviour of the blast wave from a condensed phase explosion and that from a vessel burst are illustrated in the work of Esparza and Baker (1977), who found that for the latter the blast wave tended to have a lower overpressure, a longer

positive phase duration, a larger negative impulse and a stronger second shock.

17.27.3 Vessel burst pressure

The explosion energy in a vessel burst is a function of the initial pressure, which in turn depends on the failure scenario. The higher the pressure, the larger the explosion.

Three cases may be distinguished: (1) overpressure, (2) mechanical failure and (3) fire engulfment.

If the vessel fails because it is exposed to a high operating pressure and because the pressure relief has failed, the vessel will burst at a pressure which is some factor of the design pressure, typically for mild steel a factor of 4. This is the worst case.

If a mechanical failure of the vessel occurs, which may be due to a metallurgical defect, corrosion or impact, the burst pressure will be the operating pressure.

If the vessel fails is due to fire engulfment, but with the pressure relief operating, the pressure at burst will be the accumulation pressure. This is the typical scenario of a BLEVE.

17.27.4 Vessel burst energy distribution

The estimation of the energy of the explosion in a vessel burst is discussed below, but it is appropriate first to consider briefly the distribution of this energy.

In principle, the energy available will be partitioned as energy in (1) vessel expansion, (2) vessel rupture, (3) blast and (4) fragments.

If failure is due to high operating pressure, some expansion of the vessel occurs. However, this can be neglected both because the energy is provided to the system prior to the burst and because is very small anyway.

Some energy is required to rupture the vessel, but this too is very small. The Centre for Chemical Process Safety (CCPS) gives a value of 1–10 kJ for the rupture of a pressure vessel; an explosion with 100 times this energy would still be regarded as small.

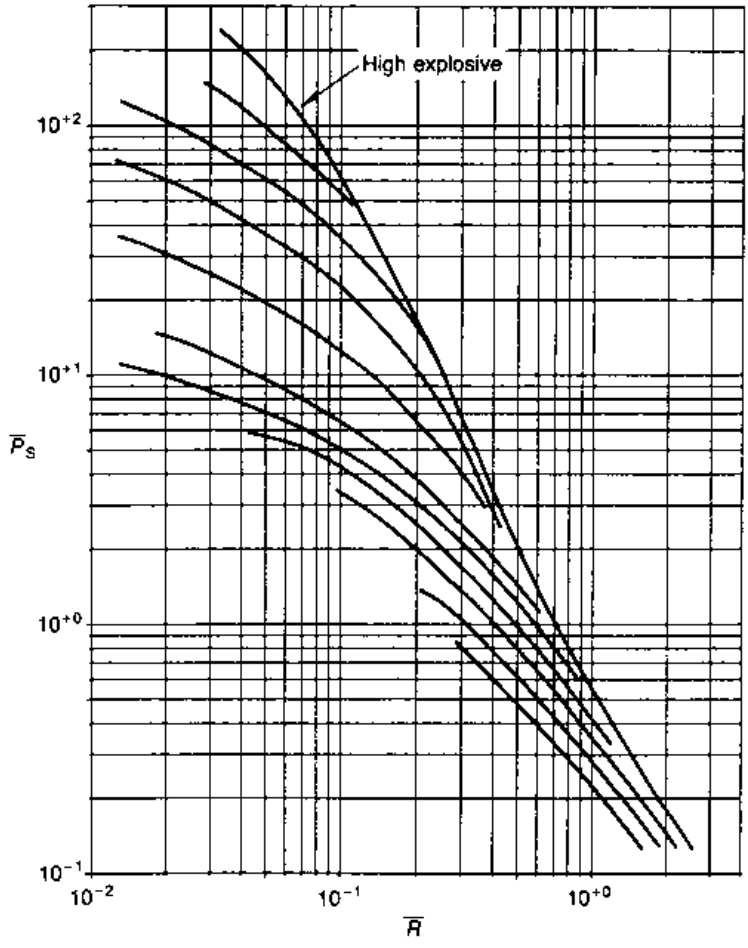


Figure 17.62 *Scaled peak side-on overpressure for a vessel burst explosion (W.E. Baker et al., 1975)*

Essentially, therefore the energy available goes into the blast and the fragments. The proportion which goes as kinetic energy in the fragments has been briefly discussed in Section 17.4 and is considered again in Section 17.34.

17.27.5. Vessel burst modelling

There have also been studies involving the numerical and analytical modelling of vessel bursts. In some cases the main interest of the work has been with other types of explosion for which the bursting of a gas-filled sphere serves as a limiting case.

Investigations involving numerical and parametric modelling have been described by W.E. Baker *et al.* (1975), Brode (1955), Adamczyk (1976), Guiraio and Bach (1979), Chushkin and Shurshlov (1982) and Raju and Strehlow (1984).

The study most relevant here is that of W.E. Baker *et al.* (1975), who conducted a parametric exploration of vessel bursts and developed a method of estimating the blast parameters analogous to that for a condensed phase explosion.

Also of interest is the work of Adamczyk (1976) which indicates that vessel burst explosions approximate in the far field to condensed phase explosions only for high pressure and temperature ratios.

The investigation by Guiraio and Bach (1979) was concerned with fuel–air explosions. They studied cases of a combustion process in which the reactants are converted instantaneously to products and found that for such cases only some 27–37% of the combustion energy was converted to work.

Raju and Strehlow (1984) studied the effect of a non-spherical source in the form of a combustible gas mixture. The initial gas cloud had the form of an ellipse rotated on its major axis, or spheroid, oriented with its major axis perpendicular to the ground. The lead shock wave was elliptical but tended towards sphericity as the wave moved out. This is explained by the facts that the strength of the initial shock wave varied with the

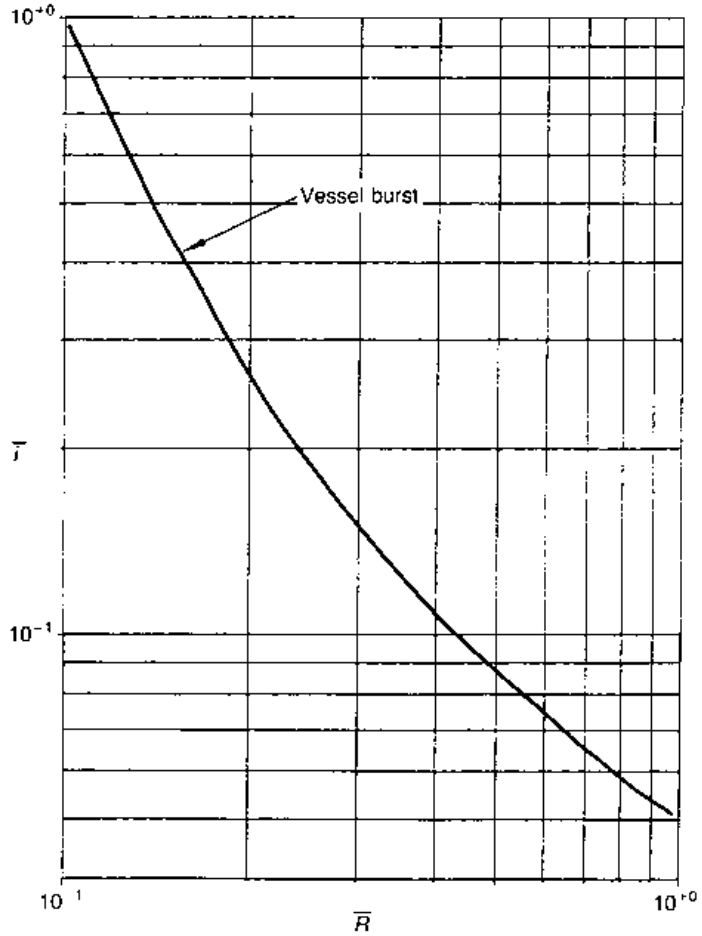


Figure 17.63 *Scaled side-on impulse for a vessel burst explosion (W.E. Baker et al., 1975)*

direction and that strong shock waves tend to travel faster than weak ones.

17.27.6. Model of Baker *et al.*: basic method

A method for the estimation of the blast parameters for the bursting of a gas-filled pressure vessel is now described. The method is that of W.E. Baker *et al.* (1975), and relates to a free-air burst of a massless spherical vessel containing an ideal gas. The background to this method has just been described and the account here concentrates on its application.

The explosion energy is obtained from the Brode model given as Equation 17.4.29.

Applying the second method of Baker and co-workers, based on Equations 17.26.7–17.26.9, the scaled distance $\bar{R}$ is calculated, using Equation 17.26.7.

The scaled peak overpressure is then obtained from Figure 17.62(a), using the curve for high explosive, and the scaled impulse from Figure 17.63, or from Figure 17.61 above, which covers a wider range.

The actual peak side-on overpressure p_s and side-on impulse i_s are then obtained from Equations 17.26.8 and 17.26.9.

This method is oriented to the estimation of the blast parameters in the far field, and its accuracy in the near field is limited. There are two checks which should be made with regard to the latter.

The first check is on the value of the scaled distance $\bar{R}$. If this is less than 2, use should be made of a modification to the method appropriate for the near field, which is described below. The other check is on the value of the peak side-on overpressure p_s, discussion of which is deferred.

The near field modification is as follows. First an effective radius for the equivalent hemisphere formed by the initial gas volume is calculated:

$$r_o = \left(\frac{3V_1}{2\pi}\right)^{\frac{4}{3}} \qquad [17.27.1]$$

where r_o is the effective radius of the equivalent hemisphere (m) and V_1 is the volume of the gas-filled vessel (m^3). The corresponding scaled distance $\bar{R}_o$ is then calculated using Equation 17.26.7.

The peak side-on overpressure is then determined using, in conjunction with Equation 17.26.8, the relation

$$\frac{p_1}{p_o} = (\bar{P}_{so} + 1)\left(1 - \frac{(\gamma_1 - 1)(a_o/a_1)\bar{P}_{so}}{\{2\gamma_o[2\gamma_o + (\gamma_o + 1)]\bar{P}_{so}\}^{\frac{1}{2}}}\right)^{-2\gamma_1/(\gamma_1 - 1)} \qquad [17.27.2]$$

where a is the velocity of sound (m/s), p_o is the absolute pressure of the ambient air (Pa), p_1 is the absolute initial pressure of the gas (Pa), $\bar{P}_{so}$ is the scaled peak side-on overpressure at $\bar{R}_o$, γ is the ratio of the specific heats and subscripts o and 1 denote ambient air and compressed gas in the vessel, respectively.

Equation 17.27.2 is an implicit equation. It may be solved by the usual methods for such equations. Alternatively, use may be made of graphs given for convenient by the authors. One of these is shown in Figure 17.64.

The method then proceeds as follows. The pair of values of $\bar{R}$ and $\bar{P}_{so}$ is used to locate the 'starting point' on Figure 17.62. This identifies a particular curve

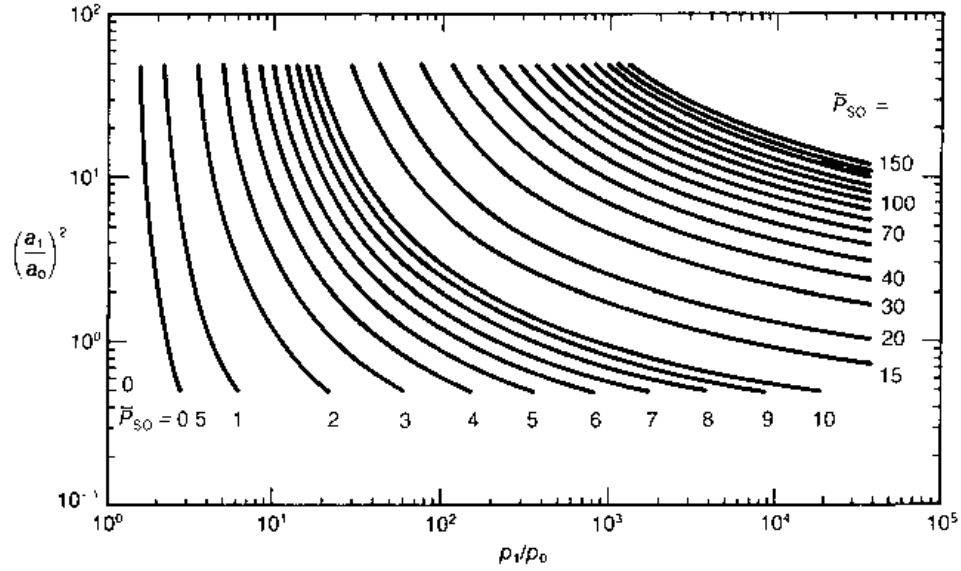


Figure 17.64 *Scaled peak side-on overpressure in the near field for a vessel burst explosion (W.E. Baker et al., 1975).* $\gamma_1 = 1.4$

in the family of curves on Figure 17.62 and this curve is then used in making further estimates of the scaled peak overpressure.

As indicated earlier there is further check to be made, on the value of the peak side-on overpressure p_s. It can occur that the value calculated for p_s exceeds the initial pressure in the vessel. If so, p_s should be set equal to this initial pressure.

17.27.7 Model of Baker *et al.*: extensions of method

As already stated, the method just described applies to the free air burst of a massless spherical vessel containing an ideal gas. There are several extensions which may be needed in practical cases. These relate to (1) non-ideal fluids, (2) energy imparted to fragments, (3) bursts at ground level and (4) other vessel geometries.

For the ideal gas case, the energy of explosion is obtained from the Brode model as given in Equation 17.4.29. For the cases of non-deal gas, vapour or flashing liquid use should be made of the alternative method described in Section 17.4.

This gives the total energy available. Any energy imparted to the fragments should then be subtracted from this value to obtain the energy participating in the blast.

For the case of a burst at ground level, this blast energy is then multiplied by the usual factor of two before it is used in Equations 17.26.7 and 17.26.9 to obtain the blast wave parameters. Baker *et al.* have given sets of adjustment factors for two types of departure from the basic model. One set is for use with cylindrical as opposed to spherical vessels. The other set is for a spherical vessel slightly elevated above the ground. These are shown in Table 17.28.

17.27.8 CCPS method

The CCPS *Fire and Explosion Model Guidelines* (1994/15) include as part of the method for a BLEVE a method for vessel burst explosions. The energy of the explosion is obtained using the CCPS method for this described in Section 17.4. The blast parameters are then obtained using the method of Baker and co-workers described in Section 17.27.6 with the extension given in Section 17.27.7. The *Guidelines* give sample problems for BLEVEs in which use is made of the vessel burst model. These problems are described in Section 17.3.29.

Table 17.28 *Method of Baker et al. for blast parameters from a vessel burst: adjustment factors (W.E. Baker et al., 1975)*

A Adjustment factors for cylindrical vessels

$\bar{R}$	*Multiplier for:* $\bar{P}_s$	$\bar{I}$
<0.3	4	2
$0.3 < \leq \bar{R} \leq 1.6$	1.6	1.1.1
$1.6 < \leq \bar{R} \leq 3.5$	1.6	1
>3.5	1.4	1

B Adjustment factors for spherical vessels slightly elevated above the ground

$\bar{R}$	*Multiplier for:* $\bar{P}_s$	$\bar{I}$
<1	2	1.6
>1	1.1	1

17.28 Vapour Cloud Explosions

When a cloud of flammable vapour burns, the combustion may give rise to an overpressure or it may not. If there is no overpressure, the event is a vapour cloud fire, or flash fire, and if there is overpressure, it is a vapour cloud explosion.

A vapour cloud explosion is one of the most serious hazards in the process industries. Vapour cloud explosions do occasionally occur and they tend to be very destructive.

A feature of a vapour cloud is that it may drift some distance from the point where the leak has occurred and may thus threaten a considerable area.

The relative importance of the vapour cloud explosion hazard has grown in recent years. Whereas in the early days of the chemical industry the largest disasters tended to be those caused by explosives, including ammonium nitrate, many of the largest disasters are now due to vapour cloud explosions.

Accounts of vapour cloud explosions include those given in *Unconfined Vapour Cloud Explosions* (Gugan, 1979), *Explosion Hazard and Evaluation* (W.E. Baker *et al.*, 1983), *Fuel–Air Explosions* (J.H.S. Lee and Guirao, 1982a) and *Major Chemical Hazards* (V.C. Marshall, 1987) and those by Brasie and Simpson (1968), Strehlow (1973b), Strehlow and Baker (1976), V.C. Marshall (1976a,c,d), Davenport (1977b, 1983), Kletz (1977d), J.H.S. Lee *et al.* (1977), Slater (1978a), Wiekema (1980, 1983a,b, 1984), J.H.S. Lee (1983), Pikaar (1983) and Rasbash (1986b).

Until the early 1980s a vapour cloud explosion (VCE) was generally referred to as an unconfined vapour cloud explosion (UVCE). However, since in combustion of a vapour cloud the occurrence of overpressure tends to occur due to the presence of structures and obstacles and of partial confinements, the term 'unconfined' is now generally omitted.

There are many gaps in the state of knowledge on vapour cloud explosions and there is no completely satisfactory theoretical model, although much progress has been made in modelling. The practical approaches tend to combine theoretical and empirical inputs.

In this section consideration is confined to the characteristics of the explosion itself. The effects of the explosion are considered below.

The energy of the explosion of a vapour cloud is normally computed as the product of the heat of combustion and a yield factor, as described in Section 17.4 and discussed further below. In this section the energy of explosion, or explosion energy, is used in this sense.

Selected references on vapour cloud explosions are given in Table 17.29.

Table 17.29 *Selected references on vapour cloud explosions*

HSE/SRD (HSE/SRD/WP28); Ministry of Defence (n.d.); Stokes (1849); Sachs (1944); G.B. James (1947–49); Whitham (1950); Toland (1957); Thornhill (1960); Glasstone (1962); Laderman, Urtiew and Oppenheim (1963); Reider, Otway and Knight (1965); Urtiew, Laderman and Oppenheim (1965); F.A. Williams (1965, 1976a, 1983); Bulkley and Jacobs (1966); Struck and Reichenbach (1967); Brasie and Simpson (1968); Strehlow (1968a,b, 1971, 1973a,b, 1975, 1981); Bach, Knystautas and Lee (1969, 1971); Benedick, Morosin and Kennedy (1971); D.J. Lewis (1971, 1980c,d); R.P. Anderson and Armstrong (1972, 1974); Ford (1972); Oppenheim, Kuhl and Kamel (1972a,b); J.A. Brown (1973); Kuhl, Kamel and Oppenheim (1973); Strehlow, Savage and Vance (1973); Beaubois and Demand (1974); Coevert *et al.* (1974); Collins (1974); Decker (1974); Geiger (1974, 1982, 1983, 1986, 1987); Munday and Cave (1974); Tanimoto (1974); Anon. (1975d); Eisenberg Lynch and Breeding (1975); Kletz (1975c,e, 1977j, 1979b, 1986l); J.H.S. Lee, Knystautas and Guirao (1975); J.H.S. Lee *et al.* (1975); Leyer, Guerraud and Manson (1975); Lind (1975); Lind and Strehlow (1975); V.C. Marshall (1975d, 1976a–d, 1977a,b,d, 1982d, 1987); Munday (1975a,b, 1976a,b, 1979); R.J. Parker (1975); Sadée (1975); Samuels and O'Brien (1975); Strehlow and Baker (1975, 1976); D.C. Bull *et al.* (1976); Gugan (1976, 1979, 1980a,b); Guirao, Bach and Lee (1976); Harvey (1976, 1979b); W.G. High (1976); Nettleton (1976, 1977c, 1980a,b, 1987); Sadée, Samuels and O'Brien (1976–77); Strehlow and Ricker (1976); Anthony (1977a); Chiu, Lee and Knystautas (1977); V.J. Clancey (1977a,c); Davenport (1977a,b, 1983); Eichler and Napadensky (1977); Fay and Lewis (1977); Hertzberg *et al.* (1977); Kolodner (1977a); J.H.S. Lee (1977, 1980, 1983b); J.H.S. Lee *et al.* (1977); J.G. Marshall (1977, 1980); Maurer *et al.* (1977); Auton and Pickles (1978, 1980); HSE (1978b, 1980 TP 7, 1981a); Slater (1978a); M.W. Taylor, Lind and Cece (1978); Benedick (1979, 1982); D. Bradley (1979); D.C. Bull (1979, 1982a,b, 1992); Girard *et al.* (1979); Nicholls *et al.* (1979); Strehlow, Luckritz *et al.* (1979); TNO (1979); Ale and Bruning (1980); van den Berg (1980, 1982, 1985); Cronenberg and Benz (1980); Diaconicolaou, Mumford and Lihou (1980); Fumarola *et al.* (1980); Geiger and Synofzyk (1980a,b); Giesbrecht *et al.* (1980); Houweling (1980); J.H.S. Lee and Moen (1980); Wiekema (1980, 1983a,b, 1984); C.W. Wilson and Boni (1980); Zalosh (1980a, 1982); Zeeuwen and Schippers (1980); Considine (1981); R.A. Cox (1981); Eidelman *et al.* (1981); Fishburn, Slagg and Lu (1981); Oran, Boris *et al.* (1981); H. Phillips (1981b, 1982, 1986, 1987, 1989); Scilly (1981); Ebert and Becker (1982); Funk *et al.* (1982); Geiger (1982, 1987); J.H.S. Lee and Guirao (1982a); Leyer (1982); Moen (1982b, 1993); Moen, Murray *et al.* (1982); Oran, Boris *et al.* (1982); Oran, Young *et al.* (1982); A.F. Roberts and Pritchard (1982); Urtiew (1982a,b); H.G. Wagner (1982); D.G. Bowen (1983); CEC (1983 EUR 8482 EN, 1984 EUR 8955 EN, EUR 9593 EN, EUR 9541 EN/I and EN/II, EUR 9592 EN); Elsworth, Eyre and Wayne (1983, 1984); Fredholm (1983); Hasegawa and Sato (1983); Hertzberg and Lamrevik (1983); Mackenzie (1983 SRD R262); Nikodem (1983); Pickles and Bittleston (1983); Pikaar (1983, 1985); Schildknecht and Geiger (1983); Spalding (1983); Urtiew, Brandeis and Hogan (1983); C.J.M. van Wingerden and Zeeuwen (1983, 1986); Benedick, Knystautas and Lee (1984); J.R. Bowen *et al.* (1984a,b); Brossard *et al.* (1984); Fry and Book (1984); M.R.O. Jones (1984); J.H.S. Lee, Kynstautas and Freiman (1984); Moen *et al.* (1984); Raju and Strehlow (1984); Schildknecht, Geiger and Stock (1984); Ungut, Schuff and Eyre (1984); Brandeis (1985); Catlin (1985); Prugh (1985–, 1987a–c); P.H.Taylor (1985a,b); Elsworth and Eyre (1986); A. Evans and Puttock (1986); Jaggers *et al.* (1986); Mudan (1986); Ogiso, Fujita and Uehara (1986); Ogiso *et al.* (1986); Pasman and Wagner (1986); Rasbash (1986b); AIChE (1987/66); van den Berg *et al.* (1987); Nettleton (1987); Skarka (1987); Giesbrecht (1988); Zeeuwen and van Wingerden (1988); Lannoy and Leroy (1989); J.B. Moss (1989); Pu, Mazurkiewicz *et al.* (1989); Puttock (1989); C.J.M. van Wingerden (1989a,b); C.J.M. van Wingerden, van den Berg and Opshoor (1989); C.J.M. van Wingerden, Opschoor and Pasman (1990); Q.A. Baker and Baker (1991); van den Berg, van Wingerden and The (1991a,b); Carnasciali *et al.* (1991); Clerehugh (1991); D.M. Johnson, Sutton and Wickens (1991); C.R. Kaplan and Oran (1991); K.G. Phillips and Henshelwood (1991); Pineau *et al.* (1991); Savvides and Tam (1991); J.E. Shepherd, Melhem and Athens (1991); Tieszen *et al.* (1991); K. van Wingerden, Visser and Pasman (1991); Buckmaster and Lee (1992); Giesbrecht *et al.* (1992); Mancini (1992); van den Berg and Lannoy (1993); Kinsella (1993); Lenoir and Davenport (1993); Leyer *et al.* (1993); Mercx, van den Berg and The (1993); Mercx, van Wees and Opschoor (1993); Madsen and Wagner (1994); K. van Wingerden, Pedersen and Wilkins (1994)

Selected experimental work

Fuel–air explosions: Kiwan (1970a,b, 1971)

Early field trials of combustion in unconfined vapour clouds: Lützke (1971); Humbert-Basset and Montet (1972); AGA (1974); MITI (1976); Raj, Moussa and Aravamuden (1979a,b)

Early work on detonation in unconfined vapour clouds: Lind (1975); D.C. Bull, Ellsworth and Hooper (1979a,b)

Combustion in unconfined vapour clouds: closely controlled tests: Lind and Whitson (1977); Deshaies and Leyer (1981); Okasaki, Leyer and Kageyama (1981); Schneider and Pförtner (1981); Brossard *et al.* (1985); R.J. Harris and Wickens (1989)

Combustion in unconfined vapour clouds: field trials: Blackmore, Eyre and Summers (1982); MIT-GRI Safety and Res. Workshop (1982); Goldwire *et al.* (1983); Hirst and Eyre (1983); Zeeuwen, van Wingerden and Dauwe (1983)

Combustion in vapour clouds with obstructions: closely controlled tests: Dörge, Pangritz and Wagner (1981); C.J.M. van Wingerden and Zeeuwen (1983); A.J. Harrison and Eyre (1986, 1987a); R.J. Harris and Wickens (1989)

Combustion in vapour clouds with obstructions – field trials: Zeeuwen, van Wingerden and Dauwe (1983)
Jet ignition of vapour clouds: Schildknecht and Geiger (1982); Schildknecht (1984); Schildknecht *et al.* (1984); Stock and Geiger (1984); Moen *et al.* (1985); A.J. Harrison and Eyre (1987a); McKay *et al.* (1988)
Combustion of turbulent jets: Seifert and Giesbrecht (1986); Stock (1987)
Combustion following vessel burst: Giesbrecht *et al.* (1981)
Combustion of a pipeline leak: Hoff (1983)

Hydrogen explosions
Bulkley and Jacobs (1966); Berman (1982); Tamm, Harrison and Kumar (1982); L. Thompson (1982); Hawksley (1986 LPB 68); V.C. Marshall (1987)

Suppression by water sprays
Acton, Sutton and Wickens (1990); D.C. Bull (1992); Brenton, Thomas and Al-Hassan (1994)

17.28.1 Vapour cloud explosion incidents

There are a number of compilations of major vapour cloud explosions. V.C. Marshall (1987) gives details of some 11 such compilations. The principal lists are those of Strehlow (1973b), Davenport (1977b, 1983), Gugan (1979), the ACMH (Harvey, 1979b), Wiekema (1983a,b, 1984) and Lenoir and Davenport (1992). The account by Davenport (1977b) also lists incidents in which a vapour cloud formed but did not explode.

It is emphasized by their compilers that the lists may be incomplete, since the extent to which incidents are reported varies between different countries. Where the lists include unignited vapour clouds, these are particularly likely to be incomplete, since such clouds are often not reported.

As mentioned above, vapour cloud explosions have come to increasing prominence. Strehlow (1973b) lists the numbers of vapour cloud explosions as follows:

1930–39, 4

1940–49, 12

1950–54, 17

1955–59, 17

1960–64, 18

1965–69, 25

1970–72 (Jan.), 15

The *Second Report* of the ACMH (Harvey, 1979b) refers to Strehlow's work and to more recent data and comments that the frequency of vapour cloud explosions has increased from about four per decade to a rate of over 60 per decade. More recent data, given in Table 2.31, suggest that the frequency of incidents has at least levelled off.

Some principal vapour cloud explosion incidents are given in Table 17.30. The estimates of the quantities released in the table are given as quoted in the literature; most appear to refer to the total quantity originally in the containment, but may in some cases refer to the flammable vapour in the cloud. Other incidents are given in Table A1.2. Further lists of vapour cloud explosion incidents illustrating particular points are given in Tables 17.33 and 17.34 below.

Four vapour cloud explosions in particular have been particularly influential. In 1967 a very destructive vapour cloud explosion occurred at the refinery at Lake Charles in Lousiana after an escape of liquid isobutylene due to a valve failure; there were seven deaths (Case History A40). The fires burned for 2 weeks. In 1968 a slops tank in the refinery at Pernis in the Netherlands boiled over and the explosion of the resultant vapour cloud killed two people and destroyed an appreciable fraction of the refinery (Case History A41). Another massive vapour cloud explosion took place in 1970 at Port Hudson, Missouri, where liquid propane leaked from a pipeline into a valley; on this occasion there were no fatalities (Case History A52).

In 1974 Flixborough in the UK a large escape of cyclohexane from a temporary pipe on a train of reactors gave rise to a vapour cloud which exploded with a TNT equivalent of some 16 te. The explosion demolished much of the works and killed 28 people, and the fires burned for over a week. This incident, which is described in Appendix 2, was particularly influential in the development of major hazard controls in the UK and in the EC.

These were not, however, the first major vapour cloud explosions. Two major explosions which occurred earlier at Ludwigshafen, Germany, in 1943 and 1948, were more destructive of human life, resulting respectively in 57 and 207 deaths. In the second incident the explosion was caused by an escape of dimethyl ether when a rail tank car overheated in the sun and burst (Case History A17). For this explosion the TNT equivalent has been estimated as 20 te.

Vapour cloud explosions have continued to occur. Also in 1974, only a few months after Flixborough, there was an escape of propane following a rail tank car accident in a marshalling yard at Decatur, Illinois, which caused seven deaths and did extensive damage (Case History A71).

In 1975 at Beek in the Netherlands an escape of propylene, apparently from brittle fracture of a feed drum on a depropanizer, gave rise to a vapour cloud explosion which killed 14 and caused extensive damage to the works (Case History A75).

One of the most serious vapour cloud explosions in recent years, however, has been that of a cloud of isobutane vapour at Pasadena, Texas, in 1989, which caused 23 fatalities and resulted in as serious a business loss as Piper Alpha. This incident, shown in Plate 38, is described in Appendix 6.

Also in 1989 there occurred at Ufa in the Soviet Union a vapour cloud explosion much more disastrous in human terms (Case History A127. Plate 37 shows the affected area after this explosion.

17.28.2 Combustion in vapour clouds

The combustion of vapour clouds in the open air was already a subject of research before the four major explosions just mentioned, but their occurrence provided a further stimulus to work on what was then generally referred to as unconfined vapour cloud explosions.

Fundamental aspects of vapour cloud explosions have been discussed by various authors, including Brasie and Simpson (1968), Strehlow (1973b), Gugan (1976, 1979), Munday (1976a,b), Anthony (1977a), V.J. Clancey (1977a), J.H.S. Lee *et al.* (1977), W.E. Baker *et al.* (1983), J.H.S. Lee (1983b), Pikaar (1983) and D.C. Bull (1992).

In the early work much attention centred on the question of detonation of the vapour cloud. Some of the problems associated with detonation are:

(1) existence of detonability limits;
(2) occurrence of unconfined detonation;
(3) direct initiation of detonation;
(4) characteristics of flame propagation;
(5) transition from deflagration to detonation.

There are in the literature statements to the effect that the limits of detonability are essentially the flammability limits. Thus, Burgess *et al.* (1968 BM RI 7196) state: 'A consensus has gradually developed that almost any gas mixture that is flammable is also detonable if initiated with a sufficiently energetic source.'

It has been shown, however, that detonability limits are in fact distinct from flammability limits, but they are more complex and more difficult to measure. Information on detonability limits for spherical detonation is especially sparse and the limits are a function of the strength of the ignition source. Detonability limits were discussed in Section 17.2 and are considered further below.

The violence of vapour cloud explosions suggests that they might well be detonations. but the occurrence of detonation as opposed to deflagration in an unconfined vapour cloud was for a long time considered to be highly unlikely, even impossible. However, in an account of the Port Hudson explosion Strehlow (1973b) stated: 'The Port Hudson explosion is a proven example of an accidental vapour-cloud detonation.' And again: 'There is no question but that detonation has occurred in accidental explosions, or that detonation can be initiated without delay in an unconfined cloud using a sufficiently strong ignition source.' He also stated: 'More commonly, the vapour cloud simply deflagrates. However, deflagration velocities are commonly observed to be quite high and extensive blast damage can occur even for this type of vapour-cloud combustion, particularly if the cloud contains a sufficiently large volume of combustible mixture at the time of ignition.'

The problem which concerned workers in this area, however, was the initiation of detonation. As Munday (1976a) commented: 'It seems highly unlikely that detonative combustion occurs in unconfined conditions unless a priming confined or condensed explosive source is ignited.'

In the Port Hudson explosion it is believed that the cloud may have been ignited by a strong ignition source in a building enveloped by the cloud.

As the debate developed in the mid 1970s there was some reversion to the view that detonation in vapour clouds is highly unlikely. There are difficulties in envisaging the mechanism by which the flame speed in an unconfined cloud can accelerate to such a degree as to reach the speeds characteristic of detonation. The consensus view developed that if detonation occurs, it is likely to be associated with special circumstances, such as the occurrence of an initiating detonation within the cloud or interaction of the blast wave with structures, resulting in flame acceleration and higher local pressures.

The *Second Report* of the ACMH (Harvey, 1979b) probably represented current opinion in stating in its discussion of the Port Hudson incident: 'Since no other single case is on record, and many deliberate attempts to detonate unconfined hydrocarbon/air clouds have failed, it would seem more justifiable to regard the occurrence of true detonation in an unconfined vapour cloud as so improbable as to be disregarded for design purposes.'

As far as direct initiation of detonation is concerned, Strehlow states that direct initiation of detonation in a vapour cloud can occur if the ignition source is sufficiently strong, and quotes experiments which demonstrate this. This has since been confirmed by further research, including both work directed to determination of detonability limits and other work directed to vapour cloud detonation as such.

It is known that flame speeds obtained in vapour clouds are greater than the normal burning velocity. Strehlow quotes a burning velocity of 9 m/s for stoichiometric hydrogen–oxygen mixtures as measured on a bunsen burner and velocities of 68–120 m/s obtained using balloons. The acceleration of the flame in a vapour cloud and the influence of factors such as apertures and turbulence has been the subject of many experiments.

It is possible that a deflagration may turn into a detonation. The dominant view has been that this is difficult to envisage in a truly unconfined situation, but the shock waves to promote the transition might arise from interaction with structures.

Although much work has been done, and continues to be done, on the detonation of vapour clouds, the focus of attention has gradually shifted to the effect of confinement on the flame and, in particular, on the conditions which promote its acceleration to very high flame speeds.

The view which emerges from this work is that significant overpressure in vapour cloud combustion tends to be associated with a degree of confinement and that the extent of this overpressure is highly dependent on the details of the confinement.

With this model the mass of flammable gas available to participate in the explosion is not the total flammable mass but that part which is within the confinement.

Another feature which is better appreciated is the importance of the initial combustion zone. This may be envisaged as a spherical zone in which the flame front expands until it breaks through the envelope of the cloud. Once this happens, relief occurs and the pressure falls. It follows from this that the overpressure developed depends on features such as cloud height and vertical confinement.

Traditionally vapour clouds have been treated as hemispherical, but in practice many vapour clouds are

Table 17.30 *Some incidents involving vapour cloud fires and explosions*

Date	*Location*[a]	*Chemical*	*Mass* released[b] (te)	*TNT equivalent*[c] (te)
1939	Newark, NJ	Butane		
1943	Ludwigshafen, Germany	Butadiene, butylene	16.5[d]	
1945	Los Angeles, CA	Butane		
1948	Ludwigshafen, FRG	Dimethyl ether	30	20
1949	Detroit, IL	Propane, butane	1.6	
1951	Baton Rouge	HCs		
1953	Campana, Argentina	Gasoline		
1954	Portland, OR	LPG	250 m^3	
1955	Freeport, TX	Ethylene	0.68–1.36	
	Wilmington, CA	Butane		
1956	Baton Rouge, LA	Butylene	10	
	North Tonawanda, NY	Ethylene	2.5	
1957	Sacramento, CA	LPG		
1958	Ardmore, OK	Propane		
	Augusta, GA	LPG		
1959	Meldrin, GA	LPG	18	
1961	Freeport, TX	Cyclohexane	18	0.025
	Lake Charles, LA	Butane		
1962	Berlin, NY	Propane	14.3	
	Fawley, UK			
	Houston, TX	Gasoline		
	Ras Tanura, Saudi Arabia	Propane	1.1	
1963	Plaquemine, LA	Ethylene		0.9
1964	Jackass Flats, NV	Hydrogen	0.09	0.027
	Liberal, KS	Propane		1.0
	Orange, TX	Ethylene	0.18	0.27
1965	Baltimore	Benzene		
	Baton Rouge, LA	Ethyl chloride	19.3	135–180
	Escambia, USA	Hydrogen, carbon monoxide	(0.070)	(0.012)
	Lake Charles, LA	Methane or ethylene		
1966	Raunheim, FRG	Methane	1–1.5	2.7
	Scotts Bluff, LA	Butadiene	0.45	
1967	Lake Charles, LA	Isobutylene	9	12
1968	Pernis, Netherlands	Light HCs	55–110	20
1969	Escombreras, Spain	Propane		(0.012)
	Fawley, UK	Hydrogen, naphtha	23	
	Glendora, MS	VCM		
	Houston, TX	Natural gas		
	Texas City, TX	Butadiene		
1970	Big Springs, TX			
	Linden, NJ	Hydrogen, HCs	114	45
	Port Hudson, MO	Propane	27–55	45
1971	Baton Rouge, LA	Ethylene	3.6	0.45
	Houston, TX	Butadiene	12	
	Longview, TX	Ethylene	0.45	0.5
1972	East St Louis, IL	Propylene	53.5	2.5
1973	Gladbeck, FRG			
	Noatsu, Japan	VCM	4.2	0.2
	St-Amand-les-Eaux, France			
	Tokuyama, Japan	Ethylene		
1974	Beaumont, TX	Isoprene	7.6	0.9
	Climax, TX	VCM	110	
	Cologne, FRG	VCM		
	Decatur, IL	Isobutane	69	20–125
	Fawley, UK	Ethylene	0.9–2.7	
	Flixborough, UK	Cyclohexane	36	18
	Holly Hill, FL	Propane		

Table 17.30 *Continued*

Date	*Location*[a]	*Chemical*	*Mass released*[b] (te)	*TNT equivalent*[c] (te)
	Houston, TX	Butadiene	<80	20–57
	Petal, MO	Butane		
	Roumania	Ethylene		
	Zaluzi, Czechoslovakia	Ethylene		
1975	Antwerp, Belgium	Ethylene	2.5	
	Beek, Netherlands	Propylene	5.5	2.2
	Cologne, FRG	Hydrogen, naphtha		
	Eagle Pass, TX	LPG	18.2	
	Rosendaal, Netherlands	Gasoline	25–50	1.0
	Watson, CA	Hydrogen	0.3	0.018
1976	Longview, TX	Ethylene		
	Los Angeles, CA			
1977	Baytown, TX	Gasoline	300	
	Brindisi, Italy	Light HCs		
	Dallas, TX	Isobutane	68.2	1.6
	Port Arthur, TX	Propane		
1978	Abqaiq, Saudi Arabia	Methane, then LPG		24
	Denver, CO	Propane		
	Immingham, UK	Syngas	0.2–0.3	0.03
	Pitesti, Roumania	Propane, propylene		
	Poblado Tres, Mexico	Natural gas		
1979	Texas City, TX	Propane	3.1	0.9
	Torrance, CA	C_3–C_4s		
	Ypsilanti, MI	Propane		
1980	Borger, TX	Light HCs		
	Enschede, Netherlands	Propane	0.11	
	New Castle, DE	Hexane, propylene	12.7	
1981	Czechoslovakia	Syngas		
	Gothenburg, Sweden	Propane	30–40 m^3	
1982	Philadelphia, PA			
1983	Port Newark, NJ	Gasoline		
1984	Romeoville, IL	Propane		
	Sarnia, Ontario	Hydrogen	0.03	0.91
1985	Cologne, FRG	Ethylene		4.1
	Edmonton, Alberta	NGL	4900 m^3	
	Lake Charles, LA	Propane		
	Mont Belvieu, TX	Ethane, propane		
1987	Pampa, TX	Acetic acid, butane		
	Ras Tanura, Saudi Arabia	Propane	300 m^3	0.9
1988	Beek, Netherlands	Ethylene		
1988	Norco, LA	Light HCs	9	
	Rafnes, Norway	VCM	25	
		Ethylene dichloride	30	
1989	Baton Rouge, LA	Ethane, propane, butane		11–14
	Minnebeavo, USSR	Propane		
	Pasadena, TX	Isobutane	37.8	
	Ufa, USSR	NGL		10 000
1990	Cincinnati, OH	Xylene, solvent		
	Maharastra, Bombay	Ethane, propane		
	Porto de Leixhas, Portugal	Propane		
	Tomsk, USSR	Gas		
1991	Kensington, GA	Butadiene		
	Pajaritos, Mexico	Propane		
	Seadrift, TX	Ethylene oxide		

[a] Further details are given in Appendix 1, including Table A1.2.
[b] Source: Lenoir and Davenport (1992).
[c] Source: Lenoir and Davenport (1992), supplemented (values in parentheses) by values from Gugan (1979).
[d] V.C. Marshall (1987).

Table 17.31 *Some experimental work on vapour cloud explosions*

A Combustion of dispersed vapour clouds

Investigators	*System*	*Gas*
A1. Work on fuel–air explosions		
Kiwan (1971a,b, 1971)		
A2. Early field trials of combustion in unconfined vapour clouds		
Lützke (1971)	Field test site	
Humbert-Basset and Montet (1972)	Field test site	LNG
AGA (1974)	Field test site	LNG
Raj, Moussa and Aravamuden (1979)	Field test site	LNG
MITI (1976)	Field test site	Ethylene
A3. Early work on detonation in unconfined vapour clouds		
Lind (1975)	Balloons	Methane, propane
D.C. Bull, Elsworth and Hooper (1979a,b)	Field test site	Methane, ethane
A4. Combustion in unconfined vapour clouds: closely controlled tests		
Deshaies and Leyer (1981)	Soap bubbles	Methane, propane, ethylene
Okasaki, Leyer and Kageyama (1981)	Soap bubbles	Ethylene
Lind and Whitson (1977)	Hemispherical balloons	Various, including methane, acetylene
Brossard *et al.* (1985)	Spherical balloons	Ethylene, acetylene
Schneider and Pförtner (1981)	Hemispherical balloons	Hydrogen
R.J. Harris and Wickens (1989)	Tent-type rig, 45 m long	Natural gas, propane, cyclohexane, ethylene
A5. Combustion in unconfined vapour clouds: field trials		
Blackmore, Eyre and Summers (1982); Hirst and Eyre (1983)	Field test site	LNG, propane
MIT-GRI (1982); Goldwire *et al.* (1983)	Field test site	LNG
Zeeuwen, van Wingerden and Dauwe (1983)	Field test site	Propane
A6. Combustion in vapour clouds with obstructions: closely controlled tests		
Dörge, Pangritz and Wagner (1981)	Apparatus with wire mesh	Methane, propane, acetylene
A.J. Harrison and Eyre (1986, 1987a)	Cylindrical sector, see Figure 17.65	Natural gas, propane
R.J. Harris and Wickens (1989)	Tent-type rig, 45 m long	Natural gas, cyclohexane
C.J.M. van Wingerden and Zeeuwen (1983)	Single plate supporting 1 cm vertical obstacles	Methane, propane, ethylene, acetylene
A7. Combustion in vapour clouds with obstructions: field trials		
Zeeuwen, van Wingerden and Dauwe (1983)	Vertical sewer pipes, diameter 1 m, height 2 m	Propane
A8. Combustion in partially confined vapour clouds without or with obstructions: work using tubes		
Chapman and Wheeler (1926, 1927)	Pipe, 50 mm diam., 2.4 m length, with orifice plates	Methane
Dörge, Pangritz and Wagner (1981)	Pipe, 40 mm diam., 2.5 m length, with orifices	Methane
C. Chan *et al.* (1980)	Pipes: (1) 63 mm diam., 0.45 length; (2) 152 mm diam., 1.22 m length; both with orifices	Methane
Moen, Lee *et* al. (1982)	Pipe, 2.5 m diam., 10 m length	Methane
Hjertager (1984)	As Moen, Lee *et al.* (1982)	Propane
J.H.S. Lee, Knystautas and Chan (1984)	Pipe, 50 mm diam., 11 m length	Hydrogen
Hjertager, Bjorkhaug and Fuhre (1988b)	As Hjertager (1984)	Propane

Table 17.31 *Continued*

A Combustion of dispersed vapour clouds – continued

Investigators	*System*	*Gas*
A9. Combustion in partially confined vapour clouds without or with obstructions: work using parallel plates		
Moen, Donato, Knystautas and Lee (1980); Moen, Donato, Knystautas, Lee and Wagner (1980)	Two plates, 2.5 m diam., with tube obstacles	Methane, hydrogen sulphide
C.J.M. van Wingerden and Zeeuwen (1983)	Two plates 0.6 × 0.6 m, with 'forest'-type obstacles	Methane, propane
Hjertager (1984)	Disc, 1 m diam., with flat and pipe-type obstacles	Methane, propane
C.J.M van Wingerden (1984)	Two plates: (1) 0.5 × 0.5 m; (2) 4 × 4 m, both with pipe rack-type obstacles	Ethylene
C.J.M. van Wingerden (1989)	Two plates 2 × 4 m, with cylindrical obstacles	Ethylene
A10. Combustion in partially confined vapour clouds without or with obstructions: work using channels		
Urtiew (1981)	Open channel, with baffles	Propane
C. Chan, Moen and Lee (1983)	Channel, variable top opening, with obstacles	Methane
Elsworth, Eyre and Wayne (1983)	Open channel, some work with baffles	Propane
Sherman *et al.* (1985)	Channel, variable top opening	Hydrogen
P.H. Taylor (1986)	Channel, variable top opening, with obstacles	Propane
A11. Jet ignition of vapour clouds		
Schildknecht and Geiger (1982); Schildknecht (1984); Schildknecht *et al.* (1984); Stock and Geiger (1984)	Enclosure, 1 × 1 × 4 m: (1) tent-type enclosure; (2) open top channel	Ethylene, hydrogen
Moen *et al.* (1985)	Balloon	Acetylene
A.J. Harrison and Eyre (1987a)	Cylindrical sector, see Figure 17.65	Natural gas
McKay *et al.* (1988)		

B Combustion of turbulent jets

Investigators	*System*	*Gas*
Seifert and Giesbrecht (1986)	Jet	Natural gas, hydrogen
Stock (1987)	Jet	Propane

C Combustion following vessel burst

Investigators	*System*	*Gas*
Giesbrecht *et al.* (1981)	Vessels, 0.226–1.0 l	Propylene

D Combustion of a pipeline leak

Investigators	*System*	*Gas*
Hoff (1983)	Gas pipeline	Natural gas

pancake shaped. Increasingly, this feature is being taken into account in studies of vapour cloud combustion.

It will be apparent from the foregoing that vapour cloud explosions are not yet well understood. Experimental studies have therefore been undertaken to improve understanding, while design approaches have been developed based on correlation of empirical features. These aspects are now described.

17.28.3 Experimental studies

There is now a considerable body of experimental work on vapour cloud explosions. Reviews include those of J.H.S. Lee (1983b), Pikaar (1985), D.C. Bull (1992) and the CCPS (1994/15).

Some experimental studies of vapour cloud fires and explosions are given in Table 17.31. A listing of experimental work suitable for the testing of vapour cloud explosion models is given by Madsen and Wagner (1994).

The review by Pikaar (1985) covers (1) release phenomena, (2) vapour cloud generation and dispersion, (3) vapour cloud combustion and (4) interactions. Vapour cloud combustion is divided into (1) combustion of premixed clouds and (2) combustion of fuel-rich clouds. The combustion of premixed clouds covers (1) combustion in open terrain, (2) influence of partial confinement and obstacles and (3) pressure waves. The interactions considered are (1) the effect of deliberate dispersion by water sprays and (2) the effective lower flammability limit following dispersion.

In his review, D.C. Bull (1992) covers large-scale work on both vapour clouds in the open and vapour mixtures in large enclosures such as modules, and gives the following classification of the research done:

State		*Phase*	
		Single	*Aerosol + hybrid*
'Unconfined'	Initially quiescent	A	B
	Initially turbulent	C	D
With congestion	Initially quiescent	E	(F)
	Initially turbulent	G	(H)
With confinement	Initially quiescent	I	J
	Initially turbulent	K	(L)
With congestion and confinement	Initially quiescent	M	(N)
	Initially turbulent	O	(P)

No large-scale work was found in the classes shown in parentheses.

The review by the CCPS (1994/15) is under the following headings: (1) unconfined deflagration under controlled conditions, (2) unconfined deflagration under uncontrolled conditions and (3) partially confined deflagration.

A Combustion of dispersed vapour clouds

A1. Work on fuel–air explosions. Much research has been done on the use of fuel–air explosion (FAE) weapons. Although this work is mainly in the military domain and unpublished, some accounts are available (e.g. Kiwan 1970a,b, 1971). Fuels used include ethylene oxide, propylene oxide, *n*-propyl nitrate and methyl acetylene/propadiene/propylene (MAPP). Further information is given by W.E. Baker *et al.* (1983).

A2. Early field trials of combustion in unconfined vapour clouds. Early work on the combustion of unconfined vapour clouds includes the field trials on liquified natural gas (LNG) described by Lützke (1971), Humbert-Basset and Montet (1972), the American Gas Association (AGA) (1974) and Raj, Moussa and Aravamudan (1979a,b) and those on ethylene by the Ministry of International Trade and Industry (MITI) (1976).

The large-scale tests on LNG carried out by Gaz de France (Humbert-Basset and Montet, 1972), described earlier, included experiments in which ignition sources were disposed at the edge of the cloud. The main purpose in this case was to obtain a cross-check on the cloud concentrations.

Tests on the explosion of ethylene–air mixtures in the open were carried out as part of the experiments, described earlier, conducted by MITI (1976) in Japan. In one test an ethylene–air mixture containing 4.08 kg of ethylene and giving a 7% mixture in air was held in a polyvinyl chloride tent and exploded by a detonator. The blast pressure was $5\,kg_f/cm^2$ at 5 m and $0.5\,kg_f/cm^2$ at 20 m distance. It was correlated by a straight line on a log–log plot of peak overpressure versus scaled distance. The TNT equivalent of the explosion was estimated as 49.2 kg. The duration time was 10 ms at 10 m distance. It was concluded that for flammable gas explosions the TNT equivalent model fits reasonably well for the peak overpressure, but that the duration time is rather longer.

A3. Early work on detonation in unconfined vapour clouds. A major theme in early research on vapour cloud explosions was the definition of the conditions under which detonation might occur.

The problem was approached from two directions. One was the study of flame speeds in unconfined clouds. Work by Lind (1975) indicated early on that flame speeds, and overpressures, in truly unconfined vapour clouds are very low.

Other work was directed to the study of the potential modes of detonation and the conditions for their occurrence. This includes research on (1) the direct initiation of detonation, (2) the deflagration to detonation transition (DDT), (3) the effect of obstructions and of partial confinement and (4) the minimum size of cloud for detonation.

Work on direct initiation of explosions has frequently utilized an explosive charge. Typical is the that of D.C. Bull, Elsworth and Hooper (1979a) on the detonation limits of ethane–air mixtures. A review of work in which detonation has been induced using an explosive charge is given by D.C. Bull (1979).

It is known that the transition from deflagration to detonation is difficult to induce in an unconfined vapour cloud, and investigations have concentrated on features which promote DDT, such as obstacles and partial confinement.

A small amount of research has been done to establish the size of cloud in which overpressures can be induced. Thus, Maurer *et al.* (1977) have shown that overpressures

can occur in even very small clouds of mass 0.5–500 kg. Fundamental approaches to the estimation of the minimum size of cloud in which detonation might occur have been described in Section 17.2. Some fundamental aspects of detonation in vapour clouds have also been discussed in Section 17.2, including DDT and minimum cloud size.

The consensus which emerged from this work on detonation in vapour clouds was that it is more fruitful to focus attention primarily on the conditions associated with high flame acceleration and high deflagration overpressure rather than on detonation as such.

A4. Combustion in unconfined vapour clouds: closely controlled tests. A number of workers have performed experiments on combustion of gas–air mixtures inside soap bubbles or balloons. They include Lind and Whitson (1977), Deshaies and Leyer (1981), Okasaki, Leyer and Kageyama (1981), Schneider and Pförtner (1981), Brossard *et al.* (1985), A.J. Harrison and Eyre (1986, 1987) and R.J. Harris and Wickens (1989). The flame speeds for gases of moderate or low reactivity obtained were low ($\leq$24 m/s) as were the overpressures ($\leq$0.06 bar), where measured.

The rig used by A.J. Harrison and Eyre (1986, 1987) is shown in Figure 17.65. It represents a sector of a pancake-shaped vapour cloud. For natural gas and propane the flame speeds and overpressures obtained in the absence of a high-energy ignition source or obstructions were low.

R.J. Harris and Wickens (1989) conducted tests in a tent-type rig of rectangular cross-section and 45 m long with a plywood floor and with polyethylene sheeting on the sides and roof. The gases used were natural gas, propane, cyclohexane and ethylene. The basic experiment was to fill the rig with a stoichiometric mixture, ignite it at one end and measure the flame speeds and overpressures generated.

One set of experiments was conducted without any obstruction of the space in the rig and without confinement of the ignition region. For this base condition the flame speeds observed were about twice those measured in the laboratory. The authors give the following data:

Gas	*Laminar burning velocity* (m/s)	*Flame speed* (m/s)	
		Laboratory tests	*Rig tests*
Natural gas	0.45	3.1	8
LPG	0.52	3.6	10
Cyclohexane	0.52	3.6	10
Ethylene	0.83	5.8	19

Thus without obstructions the flame speeds obtained were low.

The last two sets of investigators also performed experiments using obstructions, as described below.

This research has thus provided further confirmation that the flame speeds in unconfined vapour clouds of moderate or low reactivity substances are not such as to give high overpressures or detonation.

In balloon tests, high reactivity gases gave rather higher flame speeds (acetylene 38 m/s and hydrogen 84 m/s).

A5. Combustion in unconfined vapour clouds: field trials. The early 1980s saw a number of large-scale field trials on dense gas dispersion, some of which were supplemented by trials involving cloud ignition.

Accounts of this work are given by Blackmore, Eyre and Summers (1982) for trials with LNG and propane at the Maplin Sands site, Hogan (1982), MIT-GRI (1982)

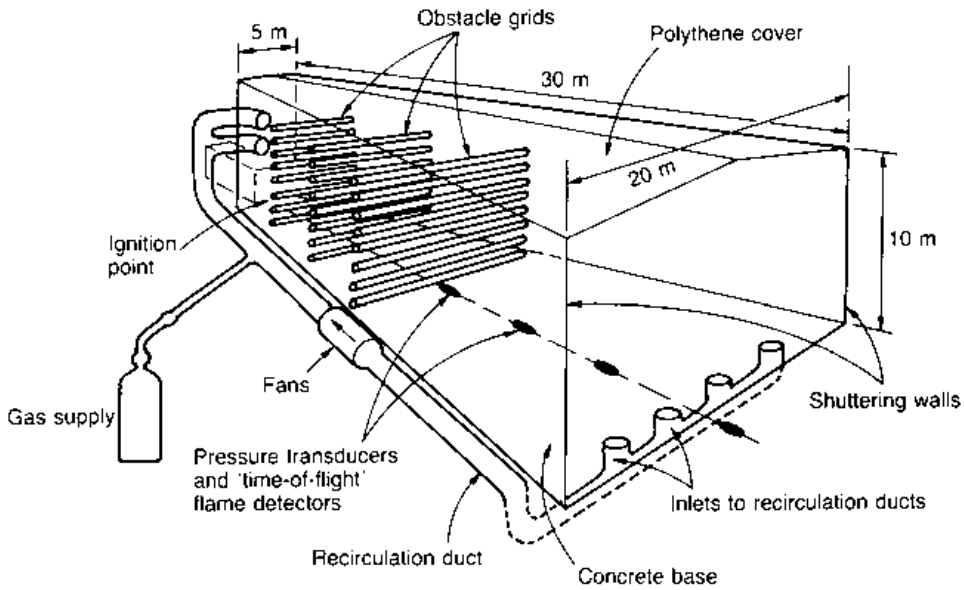


Figure 17.65 *Experimental work on vapour cloud explosions: rig representing a sector of a shallow, cylindrical cloud (A.J. Harrison and Eyre, 1986) (Courtesy of the Institution of Chemical Engineers)*

and Goldwire *et al.* (1983) for LNG trials at China Lake, and Zeeuwen, van Wingerden and Dauwe (1983) for propane trials at Musselbanks.

For LNG the maximum flame speed observed was 13.3 m/s at China Lake, and for propane 28 m/s at Maplin Sands and 32 m/s at Musselbanks.

Field trials on combustion of vapour clouds are also considered in Chapter 16 in relation to flash fires.

A6. Combustion in vapour clouds with obstructions: closely controlled tests. The absence of evidence in work on unconfined vapour clouds of flame speeds sufficiently high to give high overpressures has led to investigation of the effect of obstacles in promoting flame acceleration.

Controlled tests using obstacles have been conducted by Dörge, Pangritz and Wagner (1981), C.J.M. van Wingerden and Zeeuwen (1983), A.J. Harrison and Eyre (1986, 1987) and R.J. Harris and Wickens (1989).

The apparatus in the work of Dörge, Pangritz and Wagner (1981) contained a wire mesh, whilst that of C.J.M. van Wingerden and Zeeuwen (1983) consisted of a 60 × 60 cm plate with 1 cm vertical obstacles placed on it.

Using in their rig a blockage ratio of 40% with six grids of pipe-type obstacles, A.J. Harrison and Eyre (1986, 1987) obtained in one test on natural gas a flame speed of 119 m/s and an overpressure of 0.21 bar. They observed that the flame accelerated on entering the obstructed region and decelerated on leaving it. The tests showed that with natural gas a high degree of congestion is required to obtain high flame speeds and overpressures.

R.J. Harris and Wickens (1989) utilized the 45 m long tent-type rig already described. Again the gases used were natural gas, propane, cyclohexane and ethylene. The obstructions were placed in the central portion of the rig. The effect of these was to cause the deflagration flame to accelerate. On entering the subsequent unobstructed portion the flame decelerated again. This is illustrated in Figure 17.66(a), which shows results for cyclohexane. The flame speeds obtained were up to 10 times higher than for the unobstructed case.

Both of the last two sets of investigators studied the effect of a strong ignition source. A.J. Harrison and Eyre (1987) utilized a jet flame emerging from a partially confined region. Using natural gas, they observed in one test a flame speed of 170 m/s and an overpressure of 0.71 bar.

R.J. Harris and Wickens (1989) conducted tests with a strong ignition source using cyclohexane and propane. The tests involved the use of a central obstructed region and a modified method of ignition, obtained by confining the end region in which ignition took place. In experiments on cyclohexane the flame emerged from this region with a flame speed of about 150 m/s. The results obtained are illustrated in Figure 17.66(b), which shows that the flame ran up to detonation in the obstructed portion and that the detonation was maintained when it entered the subsequent unobstructed portion. The detonation velocity was 1700 m/s. The corresponding velocities for propane were 300 m/s leaving the confined region and 1800 m/s for detonation.

Overall, the work of Harris and Wicken illustrated the effect of a combination of fuel reactivity, ignition conditions and an obstructed region. It showed that with an obstructed region and an ignition source giving a high initial flame speed more reactive fuels can run up to detonation. On the other hand it also confirmed the much lower flame speeds associated with natural gas.

A7. Combustion in vapour clouds with obstructions: field trials. Experiments on the effect of obstacles on the course of vapour cloud explosions have also been carried out on the field scale.

Zeeuwen, van Wingerden and Dauwe (1983) have described work at TNO on field trials using obstacles which complement the small-scale work described earlier. Tests were conducted both without and with partial confinement. For the former, two types of obstacle were used: a set of large horizontal pipes and a set of sewer pipes, each 1 m in diameter and 2 m high, stood on end. The latter system, shown in Figure 17.67, consisted of seven rows of 10 pipes on a 3 m pitch. In some tests this array was open at the top and in others it was partially or totally covered. The vapour clouds consisted of 1000 kg of propane, which was introduced over a period of some 1–2 minutes through a water pond 15 m in diameter and 1 m high. The dimensions of the cloud within the flammable limits were estimated as 130 m long, 75 m wide and 2 m high. In the tests without obstacles the flame speed was generally low at 3–10 m/s, although one case was recorded of 32 m/s, and no overpressure was measured. In the tests with horizontal pipes the flame accelerated to 16 m/s at the pipes and then fell again.

In the tests with the vertical pipes uncovered the flame speed was similar to the unconfined case. In the tests with cover, the area covered was $7 \times 7\,m^2$, then $13 \times 13\,m^2$ and finally the whole array. In all but the first of these tests the flame speed increased in the covered area and decreased beyond it. With the array completely covered the flame accelerated continuously, and flame speeds of 50–66 m/s were obtained, as were maximum overpressures of 20 mbar in the cloud and 6 mbar at 75 m.

Plate 16 illustrates one of the TNO experiments with Plates 16(a)–(c) showing the movement of the flame in plan view and Plate 16(d) the elevation view.

A8. Combustion in partially confined vapour clouds without or with obstructions: work using tubes. The foregoing account indicates that the flame speed in a vapour–air mixture is affected by partial confinement as well as by obstacles. Investigators have studied a number of different geometries, notably (1) tubes, (2) parallel plates and (3) channels, the first two being representative, respectively, of one- and two-dimensional flame propagation.

Work on the behaviour of flames in tubes antedates interest in vapour cloud explosions. Early work on this topic was carried out by Chapman and Wheeler (1926, 1927) and their co-workers, using both empty tubes and tubes containing obstacles. An account of this work has been given in Chapter 16.

Combustion in tubes, especially shock tubes, is the staple of research on detonation and has been the subject of innumerable studies.

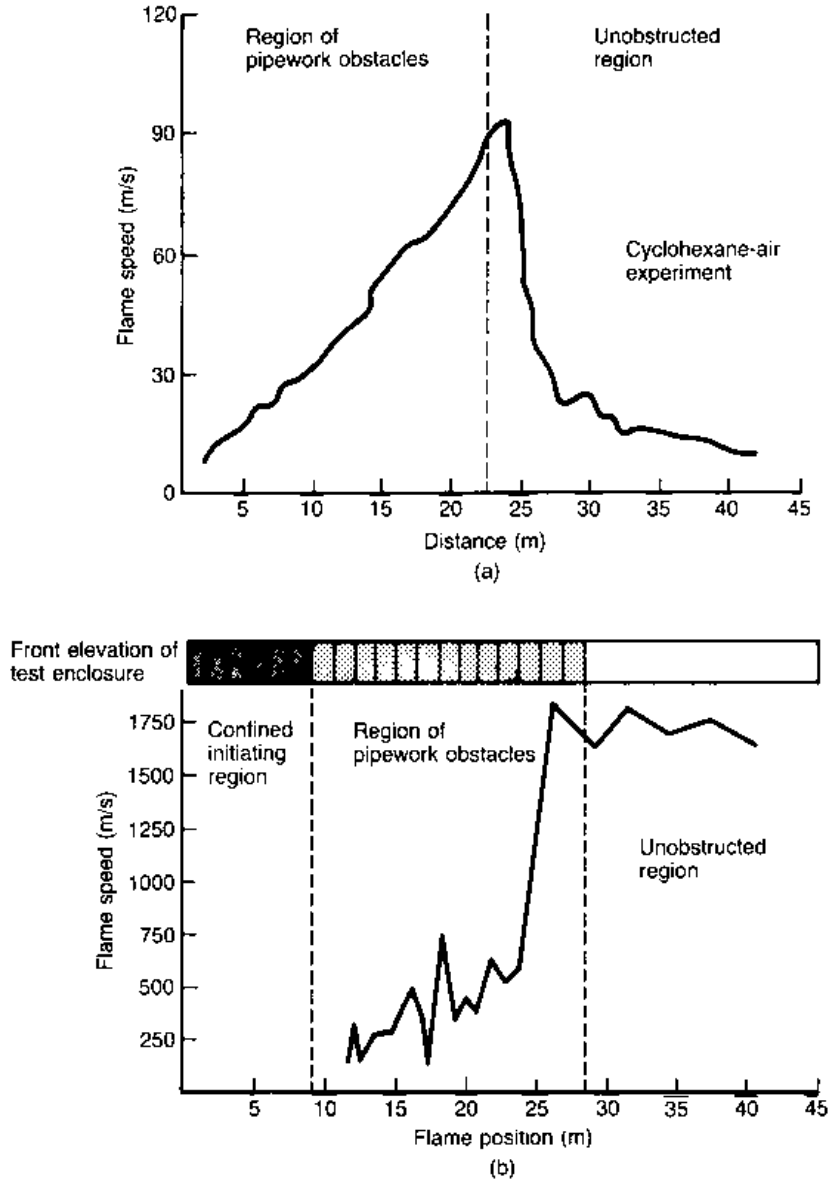


Figure 17.66 *Experimental work on vapour cloud explosions: effects of obstructions and of jet flame ignition (R.J. Harris and Wickens, 1989): (a) flame acceleration on entering obstructed region and flame deceleration on leaving it; (b) flame acceleration on entering obstructed region with transition to detonation, following jet flame ignition. Cyclohexane in both cases (Courtesy of the Institution of Gas Engineers)*

A series of investigations using tubes specifically related to vapour cloud explosions has been described by Lee, Moen, Hjertager and co-workers (C. Chan *et al.*, 1980; Moen, Lee *et al.*, 1982; Hjertager, 1984; J.H.S. Lee, Knystautas and Chan, 1985). Other work includes that of Wagner and co-workers (Dörre, Pangritz and Wagner, 1981) and Andrews and co-workers (Andrews, Herath and Phylaktou, 1990; Phylaktou and Andrews, 1991a,b).

Moen, Lee *et al.* (1982) and Hjertager (1984) carried out experiments in a pipe 2.5 m in diameter and 10 m long containing obstructions. The former obtained for methane pressures of 4 bar and the latter for propane pressures of 13.9 bar.

Subsequently, Hjertager and co-workers (Hjertager, Bjorghaug and Fuhre, 1988; Hjertager, Fuhre and Bjorghaug, 1988a) performed similar experiments with a

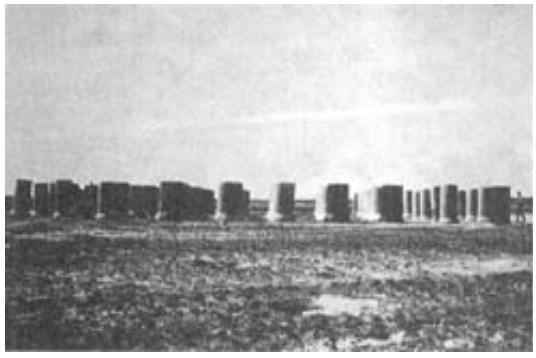


Figure 17.67 *Experimental work on vapour cloud explosions: obstacle array for field trials (Zeeuwen, van Wingerden and Dauwe, 1983) (Courtesy of the American Institute of Chemical Engineers)*

non-homogeneous mixture more representative of that from a plant leak. For non-stoichiometric mixtures the pressures obtained tended to be less than those with a stoichiometric homogeneous mixture. For non-homogeneous mixtures the pressures were equal to or less than those for homogeneous mixtures.

A9. Combustion in partially confined vapour clouds without or with obstructions: work using parallel plates. The second widely used system is a pair of parallel plates. Among the investigators who have studied this configuration are Moen, Donato, Knystautas and Lee (1980), Moen, Donato, Knystautas, Lee and Wagner (1980), C.J.M. van Wingerden and Zeeuwen (1983), Hjertager (1984) and C.J.M. van Wingerden (1984, 1989).

Moen, Donato, Knystautas and Lee (1980) used plates 60 cm in diameter with obstacles, and obtained for methane flame speeds up to 130 m/s, whilst further work by Moen, Donato, Knystautas, Lee and Wagner (1980) using 2.5 × 2.5 m plates, again with methane, gave flames speed up to 400 m/s and overpressures of 0.64 bar.

In the work of C.J.M. van Wingerden and Zeeuwen (1983), already mentioned, experiments were carried out in a closed vessel using a configuration consisting of vertical sticks held either on a single plate or between two plates. Enhancements of flame speed were observed in the confined volume, but these were much greater where the space was confined by the second, top plate. The increases in flame speed were attributed to two mechanisms. One is the stretching of the flame front as it passes through the opening between the obstacles and the other is the folding and wrinkling of the flame front due to turbulence. The authors discuss the relative importance of these two factors, which is somewhat complex.

Using a 0.5 m disc with obstructions Hjertager (1984) obtained a flame speed of 160 m/s and an overpressure of 0.8 bar for methane and a flame speed of 225 m/s and overpressure of 1.8 bar for ethylene.

In work by C.J.M. van Wingerden (1984 CEC EUR 9541 EN/II) on ethylene using 4 × 4 m plates with obstacles a flame speed of 420 m/s and an overpressure of 0.7 bar were obtained.

C.J.M. van Wingerden (1989) also used a plate apparatus to perform experiments with a range of gases of differing reactivity: methane, propane, ethylene and acetylene. He showed that reactivity can be related to the laminar flame speed and that this can be used as the basis for a method of scaling in vapour cloud explosion work.

A10. Combustion in partially confined vapour clouds without or with obstructions: work using channels. The third configuration to have attracted investigation is the channel on which work has been reported by Urtiew (1981), C. Chan, Moen and Lee (1983), Elsworth, Eyre and Wayne (1983), Sherman *et al.* (1985), P.H. Taylor (1986) and P.H. Taylor and Bimson (1989).

Working with ethylene in an open channel containing baffles Urtiew (1981) obtained a flame speed of 20 m/s.

C. Chan, Moen and Lee (1983) also used a channel with baffles and with a top containing perforations such that the degree of top confinement could be varied. For methane with high confinement a flame speed of 120 m/s was observed, but with only 10% confinement this figure fell to 30 m/s.

The experiments by P.H. Taylor (1986) also involved a perforated duct top in which the top confinement could be varied. Working with propane he obtained a flame speed of 80 m/s with a 50% blockage ratio and an 88% confinement.

Elsworth, Eyre and Wayne (1983), in tests relevant to a spill between a vessel and a jetty, investigated using an open channel the behaviour of propane systems both premixed and simulating a liquid propane spill, using baffles in some tests. The maximum flame speed in the premixed tests was 12.3 m/s.

The work on channels brings out the effect of top venting in reducing the flame speeds in vapour–air mixtures.

A11. Jet ignition of vapour clouds. Other work on vapour cloud explosions includes studies of the effect of a strong ignition source in the form of a flame jet issuing into the cloud.

Work on this form of strong ignition source by A.J. Harrison and Eyre (1987) and R.J. Harris and Wickens (1989) has been described above. It was shown to yield high flame speeds and even detonation.

B Combustion of turbulent jets

Leaving now the combustion of dispersed vapour clouds to consider that in other vapour–air release scenarios, another important case is that of the turbulent free jet. It was ignition of such a jet which gave rise to the explosion at Flixborough.

Work on this problem has been described by Seifert and Giesbrecht (1986) and Stock (1987). The former workers studied ignition of jets of methane and of hydrogen. Measurements were taken of the flame velocities and of the overpressures and duration times at different distances from the cloud.

Stock (1987) investigated jets of propane and measured overpressures within the cloud. The work included investigations of the effect of obstacles and partial confinement. For the particular configurations studied, partial confinement with 0.5 m high obstructions within 2 m high parallel walls, the overpressure in the cloud increased by a factor of about 4.

C Combustion following vessel burst

Another release scenario is that of the rupture of a vessel, reported in accounts by Maurer, Giesbrecht, Seifert and co-workers. The account by Maurer *et al.* (1977) was concerned primarily with experiments on the dispersion aspects but included some results for the overpressure from the physical burst. Giesbrecht *et al.* (1981) have described the explosion resulting from ignition of the flammable vapour cloud formed.

The experiments were done using vessels ranging in size from 0.226 to 1.0 litres, containing propylene at 40–60 bar. Figure 17.68 shows a plot of the variation of the principal variables with the initial mass in the vessel. Also shown on the plot are the extrapolations for the vapour cloud explosions at the BASF works at Ludwigshafen in 1943 and 1948 and at Flixborough in 1974.

D Combustion of a pipeline leak

Another scenario investigated is that of the ignition of a leak of flammable vapour from a pipeline. Work on this has been done by Hoff (1983).

His tests involved full bore ruptures of a 10 cm diameter gas pipeline operating at 60 bar. Ignition was effected by firing a bullet at the gas jet. The flame speeds observed were of the order of 15 m/s, and the overpressure at a distance of 50 m was measured as 1.5 mbar.

E Some factors affecting combustion of dispersed vapour clouds

It is useful at this stage to summarize some of the salient points on the combustion of dispersed vapour clouds brought out by the experimental work just described. The summary is mainly confined to qualitative observations.

Fuel reactivity. One important factor which determines the flame speeds and overpressures attained is the reactivity of the fuel.

Fuels are generally classed as being of low, moderate or high reactivity. Methane may be considered of low reactivity, ethylene of moderate reactivity and acetylene of high reactivity.

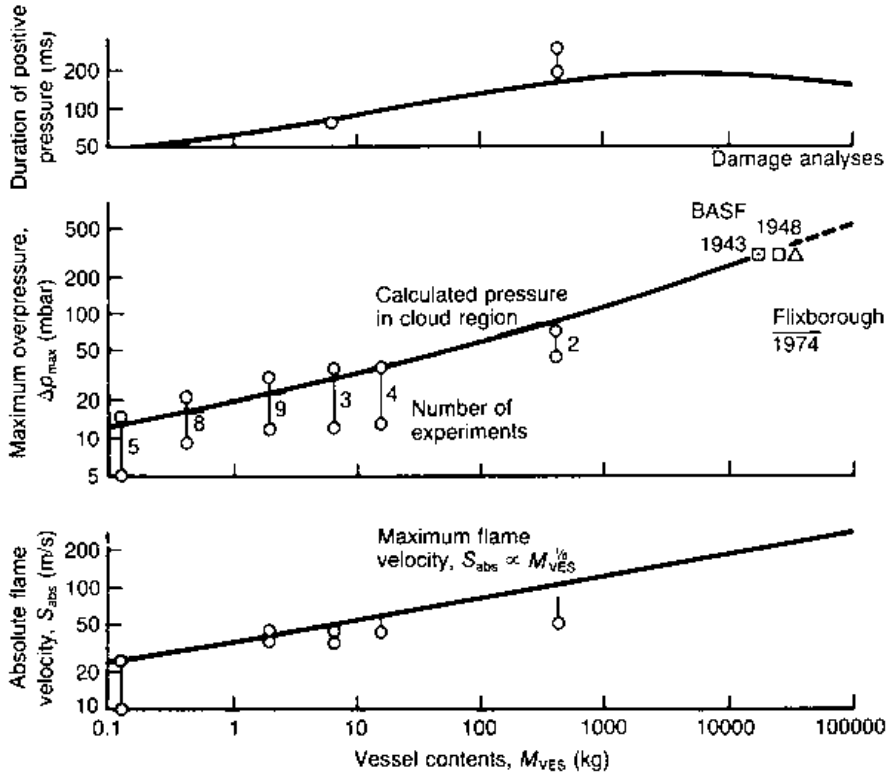


Figure 17.68 *Experimental work on vapour cloud explosions: flame velocity, peak overpressure and duration time in explosions of flammable vapour cloud formed following vessel burst (Giesbrecht et al., 1981) (Courtesy of* German Chemical Engineering*)*

A classification developed by the Factory Mutual Research Company (FMRC) (1990) from the work of D.J. Lewis (1980d) is given in Section 17.28.9. In this classification, although more reactive than methane, propane and butane are classed as low reactivity fuels.

Cloud inhomogeneity: flame speed and overpressure. The standard vapour–air mixture used in most work on vapour cloud explosions has been stoichiometric and homogeneous. Only a small amount of work has been done involving more realistic vapour–air mixtures. The work appears to indicate that whilst flame speeds tend to be lower in mixtures which depart significantly from the stoichiometric, in spaces where the mass of vapour is such that good mixing would give a mixture close to stoichiometric it is unwise to assume that the flame speed will be much reduced by a degree of inhomogeneity.

Cloud inhomogeneity: effective lower flammability limit. It has long been appreciated that due to concentration fluctuations pockets of flammable vapour–air mixture of a concentration above the lower flammability limit (LFL) may occur beyond the nominal envelope bounded by the concentration corresponding to the LFL.

It is conventional to take this effect into account by using an effective LFL and to treat that part of the cloud calculated to be within this effective LFL as potentially flammable. A common practice has been to take the effective LFL as half the actual LFL, in other words taking a peak-to-average, or P/A, ratio of 2. This is illustrated in the work of Feldbauer *et al.* (1972) used in the hazard assessment done for the First *Canvey Report*, as described in Appendix 7.

The problem has been discussed by Pikaar (1985), who points out that it may be approached either from the standpoint of gas dispersion or that of combustion. As regards dispersion, there is no doubt that the P/A concentration ratio can be high. On the other hand, combustion of vapour clouds in large field trials such as those at Maplin Sands indicates that pockets of gas can be ignited without igniting the main cloud.

The burning of a vapour cloud in the Maplin trials is shown in Plate 9.

On the basis of such considerations, Pikaar proposes the use of a P/A ratio of 1.4.

A discussion of this problem from the viewpoint of gas dispersion is given in Chapter 15.

Cloud shape. The typical vapour cloud formed by dispersion of a dense gas is pancake shaped. This has a significant effect on combustion in the cloud.

One consequence of this cloud geometry is that the gas is able to expand, or vent, through the top of the cloud, so that there is less compression of the unburned gas ahead of the flame front and the flame speed is correspondingly lower.

Another effect relates to the possibility of detonation in the cloud. There is a minimum cloud thickness for detonation to occur, this thickness being a function of the cell size, which is characteristic of the gas. For the fully unconfined case the thickness needs to be of the order of 10–13 cell sizes, whilst for the practical case of a cloud bounded by the ground it is about 5–6.5 cell sizes.

Obstructions and partial confinement. The experimental work described demonstrates that the flame speed is enhanced by the presence of obstructions, but it also indicates that the extent of this enhancement varies. For a low reactivity gas without even partial confinement the increase may be relatively limited.

The addition of partial confinement in combination with obstructions can result in a much greater enhancement of flame velocity.

Obstruction configuration. One type of obstruction which has been used by several workers is a series of grids set one behind the other at regular intervals and consisting of horizontal cylinders simulating pipework. For the particular experimental set-up, correlations have been obtained of the effect on flame speed of variables such as the blockage ratio, the spacing and the construction of the grid.

Ignition source strength. Another enhancing factor is the strength of the ignition source. The strong ignition sources principally investigated are explosives and jet flames. The effort devoted to them suggests that the latter are regarded as a credible ignition source.

Experiments on jet flame ignition have involved obstacles and some partial confinement also. They have shown that in combination with these other factors this form of ignition can give high flame speeds and in some cases detonation.

Combination of enhancing effects. The principal enhancing effects mentioned are fuel reactivity, obstacles, partial confinement and jet flame ignition. The experimental evidence suggests that these factors are most effective in producing high flame speeds, even detonation, where they are present in combination.

Water sprays. There have been a number of studies on the use of water spray to mitigate the effects of a flammable gas release by dispersing it.

Pikaar (1985) sounds a note of caution on the use of water sprays, in so far as they increase the turbulence in the cloud and could thereby make things worse. He refers to the work of Eggleston, Herrera and Pish (1976), in which flame speeds were apparently increased, although opinions differ on the interpretation of this work.

17.28.4 Empirical features

Some of the observed features of vapour cloud explosions have just been described. There are also certain empirical features knowledge of which is helpful to the designer.

A compilation of vapour cloud explosion incidents and corresponding statistical data has been presented by Davenport (1977b). These data relate to 43 incidents where overpressures were created, of which 32 were in industrial plant, eight in transport and three elsewhere. Of those in industrial plant, eight were in refineries and 24 in the petrochemical industries.

The sources of spill material in the industrial plant incidents were:

Process equipment	24
Storage tank	4
Transportation vehicle within plant	3
Unknown	1

The modes of release for all incidents were:

Vessel failure	13
Piping, valves or fittings failure	26
Release from venting facilities	3
Unknown	1

In a further paper, Davenport (1983) has given additional incidents but without statistical data.

Some questions which are capable of resolution by an empirical approach are

(1) frequency of release;
(2) quantity of material released;
(3) fraction of material vaporized;
(4) probability of ignition of cloud;
(5) distance travelled by cloud before ignition;
(6) time delay before ignition of cloud;
(7) probability of explosion rather than fire;
(8) existence of a threshold quantity for explosion;
(9) efficiency of explosion.

Early discussions of these problems were given by Strehlow (1973b), V.C. Marshall (1976a) and Kletz (1977j).

An early but fairly comprehensive treatment of the empirical features of vapour cloud explosions was given by Kletz (1977j), and this is now described. He gives estimates of the frequency of such explosions as shown in Table 17.32. A special pipeline is one on which special care can be taken, such as a short pipe without pumps or other intervening equipment between two vessels. A severe duty pump is one on a very hot or very cold liquid. The figure for pressure vessel failure is based on the data of Phillips and Warwick (1968 UKAEA AHSB(S) R162) and Engel (1974).

Table 17.32 *Estimated frequencies of vapour cloud explosion (after Kletz, 1977j)*

		Frequency (explosions/ plant-year)[a]
(1)	Caused by failure of	
	Pressure vessel	10^{-5}[b]
	Pipeline – special pipeline	10^{-5}–10^{-4}
	– normal pipeline	10^{-4}–10^{-3}
	Pump – normal pump	10^{-2}
	– severe duty pump	10^{-1}
	Reciprocating compressor	10^{-1}
(2)	Caused by leak from	
	Batch reactor	10^{-2}–10^{-1}
	Tanker filling hose	10^{-2}–10^{-1}

[a] Plant is defined as a major unit such as an ethylene or aromatics plant or collection of smaller units—something smaller than a typical UK works or US plant.
[b] The estimated failure rate of a pressure vessel is 10^{-5}/vessel-year.

On items where the frequency of leaks is high there is a strong case for an emergency isolation valve. The fitting of emergency isolation valves on a normal pipeline is usually impractical, but may well be justified on a pump. Kletz suggests that if a remotely controlled emergency isolation valve is fitted, it may be assumed that it will be operated within 5 min, but that if only a local isolation is available, it should be assumed that it will not be operated and that the leak continues until it is isolated by other means or until all the inventory has leaked out.

The material escaping may be a gas, a volatile liquid, a superheated liquid or a refrigerated liquid. It is flashing superheated liquid which tends to give rise to the largest vapour clouds. Most vapour cloud explosions have been caused by such flashing liquids. It is suggested by Kletz that the fraction vaporized be obtained from the common rule of thumb that the amount of liquid spray formed equals the amount of vapour formed by adiabatic flash. Thus if the fraction of liquid vaporized is as high as a half, this assumption implies that all the liquid turns into vapour and spray.

There are few data from which the probability of ignition can be estimated. Kletz suggests that for large leaks (>10 t) this probability is greater than 1 in 10 and perhaps as high as 1 in 2. For small leaks the probability of ignition is much less. Kletz quotes a value of 10^{-4} for small leaks on polyethylene plants, where the high pressure causes good jet mixing.

The distance drifted by a cloud of flammable vapour depends on the situation. The drift determines the explosion centre and the blast intensity near this. It has less effect on the blast intensity further away. Kletz states that there is no reported case of a cloud drifting a significant distance in a factory before exploding He suggests that the assumption of no drift is probably good enough for most calculations but that a drift of 100 m may occur in 1 case in 5 or 10. The distance drifted by the cloud before ignition is unlikely to be great in any industrial or urban area.

In open situations with few sources of ignition the vapour cloud may drift much further. In the Port Hudson explosion (NTSB 1972 PAR-72–01) the cloud travelled 1500 ft in a long plume before igniting. In the flash fire at Austin (NTSB 1973 PAR-73–04), ignition did not occur until the cloud had travelled 2400 ft. Data on the distance travelled by the vapour cloud in 81 rail tank car spills have been given by G.B. James (1947–48), who states that 58% found a source of ignition within 50 ft and 76% within 100 ft and all which ignited did so within 300 ft.

A separate but related question is the time delay before ignition. Strehlow (1973b) states that a delay as long as 15 min has been reported. The quantity of material which can accumulate in this time may be very large. The explosion can be a large one, however, even if the time delay is short. The delay before ignition

at Flixborough was probably in the range 30–90 s. An estimate of 45 s has been widely quoted.

In many instances the cloud is formed from a turbulent momentum jet. This was the case at Flixborough. In such situations the cloud may reach an equilibrium size within about 10–20 s. Once such a steady state has been reached, the mass of material available in the cloud for combustion does not increase, even if there is an appreciable delay before ignition.

The probability that ignition will cause an explosion rather than a flash fire depends on complex factors, some of which are discussed below. Kletz states that there is about one serious vapour cloud explosion every 2 years; Strehlow reports about five vapour cloud explosions/flash fires per year and these two factors in combination perhaps support the view that about one vapour cloud ignition in 10 gives an explosion.

The question of whether there is a minimum size of cloud below which an explosion will not occur has been much discussed, and a threshold quantity of 10–15 t has been suggested.

A number of vapour releases have been analysed by V.C. Marshall (1976a), as shown in Table 17.33. The table indicates that whereas the larger releases have resulted in explosions, the smaller ones have produced fires instead. The data given show no explosions in clouds of less than 15 t. Marshall has also pointed out, however, that the explosion at Beek in 1975 involved a release of only about 5.5 t and therefore tends to undermine this argument. In addition, the data of Davenport (1977b) include a number of explosions of vapour clouds containing less than 15 t of flammable material.

It is argued by Kletz that there is no theoretical basis and no detailed survey to support the assumption that there is a threshold quantity for an explosion to occur. In one well attested case a fraction of a ton of methane exploded, causing serious damage. Moreover, there have been a number of experiments with balloons filled with flammable mixtures in which violent explosions have been obtained with quantities of less than 1 t. Kletz concludes that although it may not be correct to assume a threshold quantity, the probability of an explosion certainly appears to be much less if the quantity is small. He suggests that if there are 10 t of vapour, the probability of explosion is at least 1 in 10, whereas if there is 1 t or less the probability of explosion is of the order of 1 in 100, or, more likely, 1 in 1000.

The ratio of the energy in the blast wave to the energy theoretically available from the heat of combustion, or efficiency of explosion, is another quantity about which much uncertainty exists. The fraction of the heat of combustion that is used to produce the blast wave usually lies between 1 and 10%.

The Bureau of Mines is sometimes quoted as recommending the use of an explosion efficiency of 10%. Kletz points out, however, that this should be taken in conjunction with another recommendation that the quantity of material considered should be that leaking within 30 s.

Kletz suggests that if the release if fairly rapid, it is reasonable to assume an explosion efficiency of 1%, whereas if it is not, an overall efficiency becomes meaningless and it is necessary to attempt to calculate the amount within the flammable range.

Burgess and Zabetakis (1973 BM RI 7752) have given such a calculation for the Port Hudson explosion (Case History A52).

In some cases a much higher explosion efficiency has been reported. Davenport gives an explosion efficiency of 25–50% for a vapour cloud explosion at Decatur, Illinois, in 1974 but this value may well be anomalous; it is discussed in the account of the incident (Case History A71).

Values of the explosion efficiency, or yield factor, are not always quoted on the same basis, and this is a cause of variation in the figures. Sometimes the value quoted is based on the total amount of vapour in the cloud and sometimes on that part of the vapour which is within the flammable range. The two may differ by a factor of 10 or

Table 17.33 *Some data on quantity released and on occurrence of fire or explosion in vapour clouds (after V.C. Marshall, 1976a)*

Location	*Date*	*Chemical* (t)	*Quantity*	*Deaths*	*Nature of incident*	*Further details*
Pernis, Netherlands	1968	Mixture of hydrocarbons	140	2	Explosion	Slopover
– –		Butane	77		Explosion	
– –		LNG	53		Explosion	
Lake Charles, La.	1967	Isobutane	46	7	Explosion	Accidental opening of large valve
– –		Propylene and propane	40		Explosion	
Port Hudson, Miss.	1970	Propane	29	0	Explosion	Pipeline break
Flixborough, UK	1974	Cyclohexane	25	28	Explosion	Process pipe break
–	–	Butane	15.5		Fire	
–	–	Butane	7.7		Fire	
Los Angeles, Calif.	–	Butane	2.0		Fire	
–	–	Methane	1.0		Fire	
–	–	Propane	0.06		Fire	

more. Thus, Kletz points out that although the yield factor at Port Hudson is widely quoted as being 20%, this is based on the part of the cloud which was within the flammable range. Based on the whole cloud the value is 7.5%. Further variability is introduced by the fact that the total quantity of vapour released is generally subject to uncertainty. A typical factor of uncertainty is two.

Kletz' account of the empirical features of vapour cloud explosions is intended primarily as a guide to plant design. It may be regarded as an integrated treatment such that using the various empirical values given the result obtained is reasonable. The application of the values may be less valid if used as part of an eclectic approach.

Kletz (1979b) has applied this approach to obtain guidance on plant layout. This was described in Chapter 10.

More recently, Wiekema (1984) has carried out a statistical study on some 165 vapour cloud ignitions. Incidents were not included where no ignition occurred or where ignition was virtually simultaneous with the release, as in a BLEVE. On the other hand, no incident was excluded simply because some information on it was lacking. The study is based on reported incidents and, as the author points out, is therefore a biased sample.

The features selected for analysis are given under the following headings: (1) mass, (2) reactivity, (3) ignition source, (4) drift, (5) explosion, (6) location, (7) delay, (8) fatalities, (9) injured and (10) domino effects. The gas is classed as being of high, medium or low reactivity; the ignition sources as continuous or non-continuous; the combustion as a flash fire or explosion; the location as containing obstacles and therefore being semi-confined or as being free from obstacles and not semi-confined; and the situation as one where vulnerable objects were absent and a domino effect was not possible, where such objects were present and a domino effect occurred and where such objects were present but no domino effect occurred.

The results of the survey are shown in Figure 17.69. Since for many incidents some information was lacking, the number of cases given for each of the subfigures varies. Most of the releases were of medium reactivity materials. For these the analysis gave the results shown in Table 17.34.

Wiekema draws from his analysis the following conclusions:

(1) In 87 out of 165 incidents the distance within which ignition occurred was known. More than 60% of these 87 vapour clouds were ignited within 100 m from the location of the spill. In only 2% of these cases did the vapour cloud drift more than 1 km before ignition took place.

(2) In 150 out of 165 incidents it was known whether an explosion or flash fire occurred. In nearly 60% of these cases the ignition resulted in an explosion; in the other cases a flash fire occurred.

(3) In 143 out of 165 incidents the number of fatalities was known. In about 40% of these cases there were no fatalities and in 25% no one was hurt.

(4) The amount spilled did not influence the probability of an explosion for the investigated incidents in the spill range 1–100 te.

(5) Explosions occurred only in semi-confined situations and never in unconfined situations.

(6) A short delay time to ignition enhanced the probability of an explosion.

(7) For delay times to ignition larger than half-an-hour only flash fires occurred.

(8) Outside the combustible cloud no one was killed due to primary blast effects.

Table 17.34 *Some principal statistical features of ignited vapourclouds of material of medium reactivity (after Wiekema, 1984) (Courtesy of Elsevier Science Publishers)*

	Explosion		*Flash fire*	
	No.	*(%)*	*No.*	(%)
Mass (kg):				
$<10^2$	0	3	1	4
10^2–10^3	6	14	3	12
10^3–10^4	15	43	10	38
10^4–10^5	12	31	7	27
$>10^5$	3	9	5	19
Ignition:				
continuous	13	65	12	55
not continuous	7	35	10	45
Drift (m):				
$<10^2$	16	55	19	61
10^2–10^3	12	41	11	35
$>10^3$	1	4	1	4
Location:				
semiconfined	37	100	15	65
unconfined	0	0	8	35
Delay (min):				
<1	5	25	3	14
1–5	7	37	10	48
6–15	5	25	3	14
16–30	3	16	0	0
>30	0	0	5	24
Fatalities:				
0	21	39	24	50
1–5	19	35	17	36
6–15	8	15	5	10
16–50	5	9	2	4
>50	1	2	0	0
Injured:				
0	7	15	15	44
1–5	10	22	12	35
6–15	9	20	3	9
16–50	11	24	3	9
>50	9	20	1	3

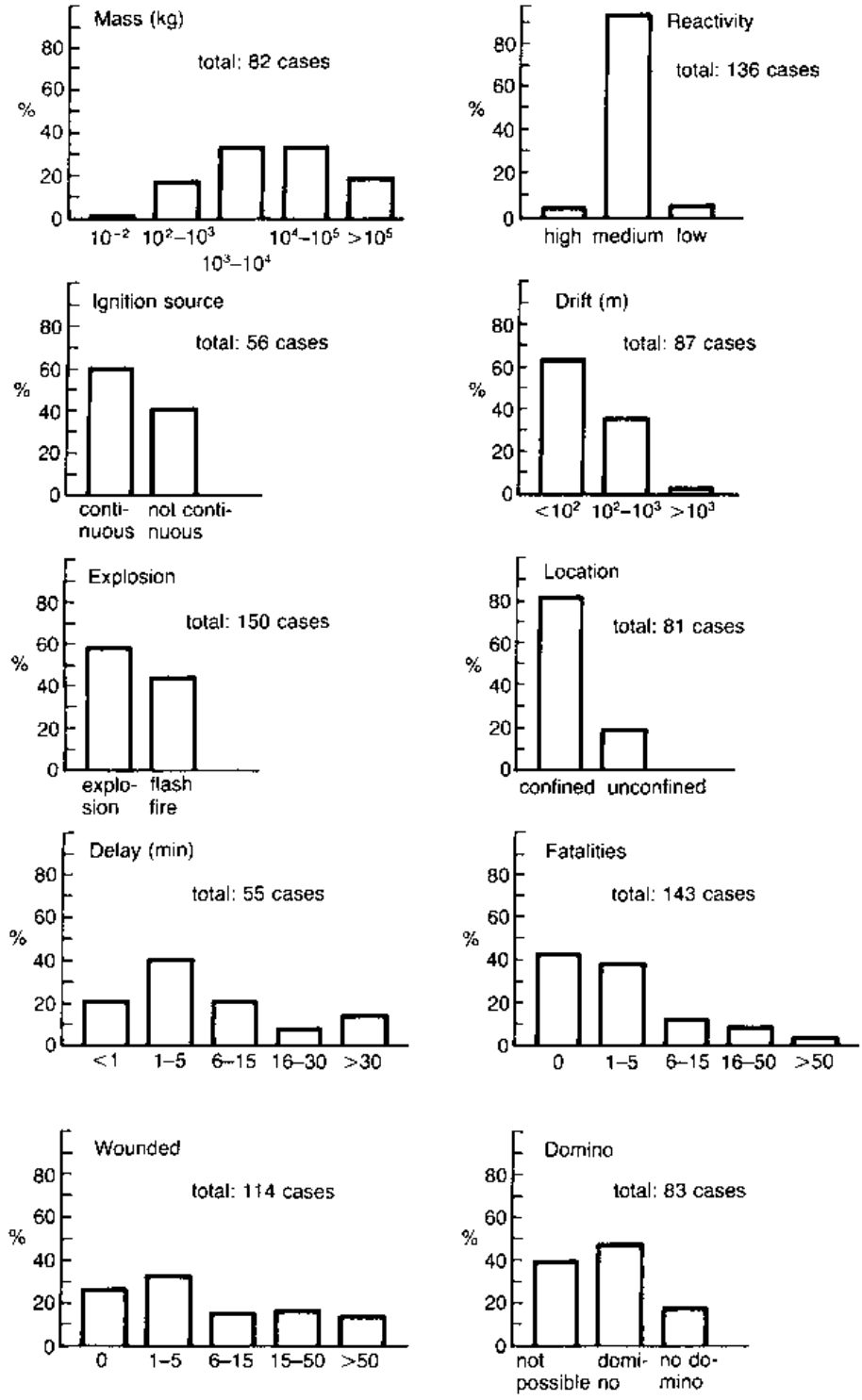


Figure 17.69 *Histograms showing selected features of a vapour cloud explosion (Wiekema, 1984) (Courtesy of Elsevier Science Publishers)*

(9) For flash fires the number of injured was of the same order as the number of fatalities. For explosions the number of injured was one order of magnitude larger than the number of fatalities.

Vapour cloud explosion is one of the hazards considered in the two *Canvey Reports*. The treatment given in these reports is described in Appendix 7.

17.28.5 Vapour cloud explosion modelling

Although there are many gaps in the understanding of vapour cloud explosions, considerable progress has been made in modelling such explosions.

Work on fundamental models has been described by a number of authors, including G.I. Taylor (1946), F.A. Williams (1965), Kuhl, Kamel and Oppenheim (1973), Strehlow (1975, 1981), Munday (1975a,b, 1976a,b), Gugan (1979), Wiekema (1980), W.E. Baker *et al.* (1983) and van den Berg (1985).

Other work has been directed to the correlation of experimental results and to the development of semi-empirical models. This includes the work of C.J.M. van Wingerden (1989), C.J.M. van Wingerden, van den Berg and Opschoor (1989) and C.J.M. van Wingerden, Opschoor and Pasman (1990) and of K. van Wingerden, Pedersen and Wilkins (1994).

Some of the approaches taken to modelling have been described by Munday (1976a). These are:

(1) point source models –
  (a) TNT equivalent model,
  (b) self-similarity model;
(2) fuel–air cloud model;
(3) bursting vessel model;
(4) piston model –
  (a) constant velocity piston model,
  (b) accelerating piston model.

In the TNT equivalent model the explosion is taken to be equivalent to that of a TNT explosion with the same energy of explosion. This model is therefore an empirical one, but it was for some time virtually the only practical model available. It was considered in Section 17.26 and is discussed further below.

The TNT equivalent model has a single parameter, the mass of TNT. It can be made more flexible by the introduction of a second parameter, the height above ground zero at which the explosion occurs. The effect of increased height is to reduce the overpressures near the centre. The use of an arbitrary assumed explosion height is useful in obtaining better fits to overpressures assessed from damage in actual explosions.

In the self-similarity model, the blast parameters such as peak overpressure are correlated in terms of the ratio radial distance/time. In its simplest form the model gives a power law relation for the variation of peak overpressure with distance.

In the fuel–air cloud model it is assumed that a detonation propagates through the fuel–air mixture without any expansion of the cloud. A shock wave with a high peak overpressure is produced at the cloud boundary. With combustion thus complete, subsequent decay of the shock wave is similar to that for the point source models.

Another approach is to assume that the fuel–air mixture undergoes combustion in a hemispherical vessel, defined by the cloud boundary, and that when combustion is complete, the vessel bursts. The state of the gas, after combustion but before bursting, is determined by standard methods. Subsequent decay of the shock wave may be calculated by numerical solution of wave propagation equations.

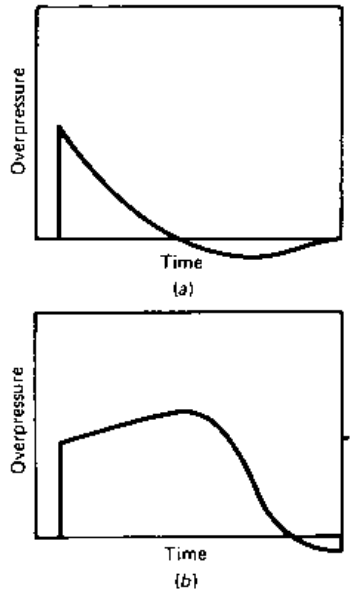


Figure 17.70 *Variation of overpressure with time in TNT equivalent and constant velocity piston models of an vapour cloud explosion (after Munday, 1976a): (a) TNT equivalent model; (b) constant velocity piston model (Courtesy of the Institution of Chemical Engineers)*

A widely used method has been to treat the flame front as a constant velocity piston. Early work on the piston model was done by G.I. Taylor (1946). This approach has been taken forward by Kuhl, Kamel and Oppenheim (1973), Strehlow (1981) and other workers.

Figure 17.70 illustrates the variation of the overpressure with time in the TNT equivalent model and constant velocity piston models of a vapour cloud explosion.

The constant velocity piston approach has also been used by Wiekema (1980) at TNO. His model is a practical one and is quite widely used. It is described below.

Van den Berg (1985) at TNO has developed this work to produce a multi-energy model, also described below, which reflects the fact that the main energy release is from the confined parts of the cloud.

Finally, TNO have presented an empirical model for the damage circles caused by a vapour cloud explosion.

Before considering these models, however, mention should be made of several other concepts which are important in modelling.

One of these is that of flame acceleration. Some of the factors which influence this have been considered by C.J.M. van Wingerden and Zeeuwen (1983) in their work on the influence of obstacles. They describe two effects which enhance flame speed. One is the stretching of the flame front as it passes through an opening. The flame front velocity V_f is

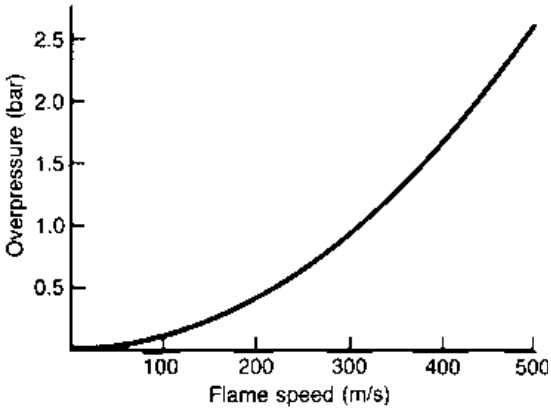


Figure 17.71 *Overpressure in a vapour cloud deflagration as a function of flame speed (R.J. Harris and Wickens, 1989; after Kuhl, 1981) (Courtesy of the Institution of Gas Engineers)*

$$V_f = \frac{\rho_u S}{\rho_b} \quad [17.28.1a]$$

$$= \frac{\rho_u}{\rho_b}\frac{A_f S_L}{A_o} \quad [17.28.1b]$$

where A_f is the disturbed flame surface area, A_o is the undisturbed flame surface area, S is the burning velocity, S_L is the laminar burning velocity, ρ is the gas density and the subscripts b and u denote burned and unburned.

For the case where this effect, rather than that of turbulence, is the dominant factor a simple relation may be derived for the flame acceleration. If the flame front velocity is V_{fo} before an obstacle and V_{fl} after it, then

$$V_{fl} = V_{fo}(1 + \Delta A/A) \quad [17.28.2]$$

where $\Delta A/A$ is the relative increase in flame surface area. Hence the flame front velocity V_{fn} after n obstacles is

$$V_{fn} = V_{fo}(1 + \Delta A/A)^n \quad [17.28.3]$$

with

$$n = r/p \quad [17.28.4]$$

or, if the flame front velocity V_{fo} entering the obstacles is some multiple α of the base value V_L,

$$\frac{V}{V_L}(r) = \alpha(1 + \Delta A/A)^{(r-r_o)/p} \quad [17.28.5]$$

where p is the pitch, r the radius of the flame front and r_o its radius at the entry to the obstacles.

Another basic concept is the relation between the flame velocity and the overpressure generated. This has been derived by several workers. Figure 17.71 shows a typical plot of this relation.

17.28.6 Mass of fuel

The estimation of the mass of fuel within the flammable range in the vapour cloud is not entirely straightforward.

For a defined release scenario the mass of fuel within the flammable range may be estimated using gas dispersion models. This is discussed in Chapter 15.

Many of the expressions given are based on models for neutral density gas. Treatments using on such models have been given by Burgess *et al.* (1975), Eisenberg, Lynch and Breeding (1975), V.J. Clancey (1977a), van Buijtinen (1980) and J.G. Marshall (1977, 1980).

Generally, dense gas dispersion models will be more appropriate. The typical dense model is a box or slab model in which the gas cloud is defined in terms of its radius and height. The model may be a box model in which the gas concentration within the cloud is assumed to be uniform. In such a model the available mass of fuel remains constant, until the concentration falls below the lower flammability limit. Or the model may be a slab model in which the variation of concentration with distance is taken into account so that the available mass of fuel changes with time.

Some problems concerning the definition of the mass of fuel have been identified and discussed by R.A. Cox (1981). He reviews the merits of basing estimates on the mass within the flammable range, or flammable mass, or the total mass released. The ratio of the flammable mass to the total mass released is likely to be highly variable. It will be small for a large inventory escaping through a small hole, but may be as high as half for an instantaneous burst. In view of this variability the blanket application of a single explosion efficiency is not likely to give accurate results.

Cox discusses but dismisses suggestions that there may be lower and upper limits to the size of cloud which can explode. He draws attention to the Badische Anilin und Soda Fabrik (BASF) work, mentioned above, which shows that overpressures can be induced in clouds of 0.5 kg mass. As for the suggestion of an upper limit of 50 te, he concludes that there is no real evidence for this either.

Cox draws attention to the fact that where the release is a turbulent jet there may be entrainment into the jet of fuel from outside the flammable envelope. In the absence of such entrainment the mass in the cloud is often quite modest, but it can be appreciably enhanced by entrainment.

Various authors have developed procedures for the determination of the size of the vapour cloud, generally for design purposes and frequently for use with a TNT equivalent model. Some of these are described in Chapter 15.

17.28.7 Energy of explosion

The energy of explosion in a vapour cloud explosion is usually only a small fraction of the energy available as calculated from the heat of combustion. This point has already been discussed in Section 17.4. As stated there, the explosion efficiency, or yield factor, may be quoted on the basis of the total mass released or of the flammable mass. Although the latter is the more fundamental basis, the former is the more convenient and the more common.

Values of the yield factor in vapour cloud explosions discussed by Kletz were quoted in Section 17.27.4.

The *Second Report* of the ACMH (Harvey, 1979b) discusses the location and design of works buildings, and in this context suggests that an yield factor of 3% be provisionally assumed.

In some cases a much higher yield factor has been reported. Davenport gives a yield factor of 25–50% for a vapour cloud explosion at Decatur, Illinois, in 1974. Similarly, Gugan (1979) quotes for this case a yield factor of 32–65%. This anomaly has been examined by V.C. Marshall (1980d), who concludes that the TNT equivalent quoted is not well founded, being based on a small number of damage points which lie well within the scatter of points obtained for the Flixborough explosion. He presents evidence of damage to support the view that the strength of the explosion at Decatur was not more, and was probably less than, that at Flixborough.

The yield factor is discussed further in Section 17.28.14.

17.28.8 TNT equivalent model

As mentioned above, the TNT equivalent model has been widely used to model vapour cloud explosions. An early application was that of Brasie and Simpson (1968), who used it to study the damage from three accidental explosions.

The TNT equivalent model was also used by Sadée, Samuels and O'Brien in their investigation of the vapour cloud explosion at Flixborough. In this case a two-parameter model was used, utilizing the height of the explosion as well as the mass of TNT. This work is described in Appendix 2.

There are, however, important features of a vapour cloud explosion which differentiate it from one of TNT. These include (1) the large volume of the cloud, (2) the lower overpressure at the explosion centre, (3) the different initial shape of the blast wave and (4) the longer duration time of the blast wave.

A discussion of these characteristics has been given in the *Second Report* of the ACMH (Harvey, 1979b). The report gives the following estimate for the size of the vapour cloud in the Flixborough explosion:

Flixborough	$0.5 \times 10^6\,m^3$
St Paul's Cathedral (internal volume)	$0.2 \times 10^6\,m^3$

The overpressure at the explosion centre of a vapour cloud is much less than at that of a TNT explosion. The report suggests that a theoretical upper limit might be calculated related to the pressure which would be achieved if the equivalent mass of TNT after detonation were confined within particular boundaries under adiabatic conditions. For a TNT explosion the boundaries would be those of the TNT charge and the pressure developed would be about 0.5 million bar. For a vapour cloud explosion the boundaries would be those of the cloud and the pressure developed would be about 8 bar. In both cases the practical upper limit of overpressure would be some fraction of the theoretical maximum value, particularly for a vapour cloud. The report suggests that on the basis of the rather meagre data available the practical upper limit is probably about 1 bar at the centre and about 0.7 bar at the boundary of the cloud.

The overpressure at the explosion centre at Flixborough may have been about these values, as discussed in Appendix 2.

In a vapour cloud explosion the shape of the initial blast wave is different from that in a TNT explosion. But it is frequently assumed that after the blast wave has travelled a certain distance it becomes indistinguishable in form from the wave of a TNT explosion. In other words, it assumes the shape shown in Figure 17.57.

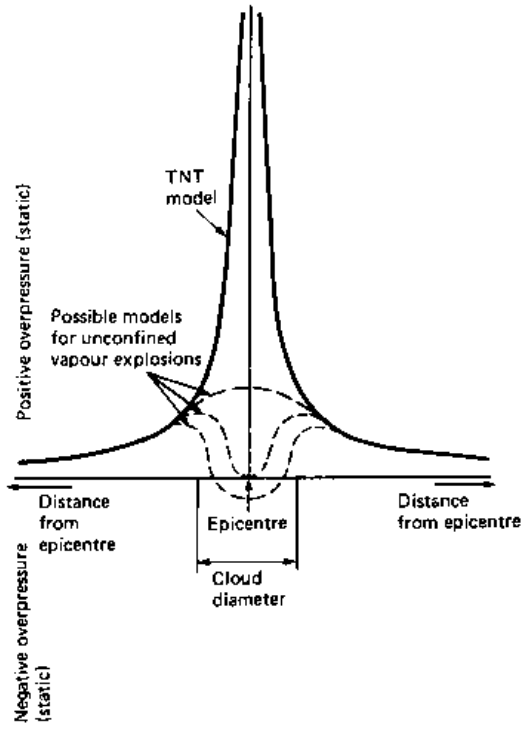


Figure 17.72 *Overpressures given by the TNT equivalent model and by some possible models of vapour cloud explosion (V.C. Marshall, 1976c) (Courtesy of the American Institute of Chemical Engineers)*

The shape of the overpressure profile according to the TNT equivalent model and to some possible models of vapour cloud explosions is shown in Figure 17.72.

The apparent TNT equivalence of a vapour cloud explosion changes with distance. In the far field the quantity of TNT required to obtain a fit for the overpressure is tends to be appreciably higher than in the near field.

The blast wave from a vapour cloud explosion also differs from that of a TNT explosion in duration time. The duration time of a vapour cloud explosion is generally considered to be appreciably longer than that of the equivalent TNT explosion.

Thus, TNT gives a 'hard' explosion with high overpressure and short duration time, whilst a vapour cloud gives a 'soft' explosion with low overpressure and long duration time. The lower overpressure reduces the relative destructiveness but the longer duration time increases it.

There is, however, little information on the duration time for vapour cloud explosions. This is a serious deficiency, because a knowledge of duration time is needed for the design of works buildings.

The *Second Report* of the ACMH suggests, in the context of the design of works buildings and in

conjunction with the assumed overpressure of 1 bar at the cloud centre, that a duration time of 30 ms be provisionally assumed.

The TNT equivalent model has been widely applied to vapour cloud explosions, as described by van den Berg (1985). It is one of the types of model used in the CCPS methodology. It also has its critics, who regard it as obsolete. An example of this viewpoint is the account by Pasman and Wagner (1986).

17.28.9 TNT equivalent models: influencing factors and special features

Some of the various TNT equivalent models developed tend to emphasize a particular influence on or feature of vapour cloud explosions. These include (1) the reactivity of the fuel, (2) the effect of cloud size, (3) effect of obstructions, (4) the variation of TNT equivalence with distance and the (5) the peak overpressure at the edge of the cloud. The treatments of these factors are of value quite apart from their use in the particular models.

For the reactivity of the fuel, the FMRC (1990) has developed the following classification, based on the work of D.J. Lewis (1980d):

Class	*TNT equivalence*
I Relatively unreactive materials (e.g. propane, butane and ordinary flammable materials)	5%
II Moderately reactive materials (e.g. ethylene, diethyl ether, acrolein)	10%
III Highly reactive materials (e.g. acetylene)	15%

In the method given by Prugh (1987a) the effect of cloud size is taken into account by making the yield of the explosion a function of the mass of fuel in the cloud.

Two different approaches to the effect of obstructions are used in the methods of Exxon (n.d.) and R.J. Harris and Wickens (1989). In the Exxon method a distinction is made between a cloud in the open and one in partially obstructed terrain. In that of Harris and Wickens the mass participating in the explosion is limited to that in the part of the cloud in the obstructed area.

The variation of TNT equivalence with distance is taken into account by Prugh (1987a) by the use of a virtual distance method in which the virtual distance is a function of the mass of fuel involved in the explosion. The effective distance is then the sum of the virtual distance correction and the actual distance; by this expedient he obtains a single curve to fit the far field overpressures and approximate those in the near field.

The concept of virtual distance is also utilized by R.J. Harris and Wickens (1989), but in this case to obtain a match for the peak overpressure at the edge of the cloud.

All these approaches have something to offer, but there does not appear to any single method which incorporates them all.

17.28.10 TNT equivalent models: Brasie and Simpson model

The basic TNT equivalent model was stated in a classic paper by Brasie and Simpson (1968). Their expression for the TNT equivalent is now generally written in the form

$$W_{\mathrm{TNT}} = \alpha \frac{W\,\Delta H_{\mathrm{c}}}{E_{\mathrm{TNT}}} \qquad [17.28.6]$$

where E_{TNT} is the energy of explosion of TNT (kJ/kg), ΔH_{c} is the heat of combustion of the hydrocarbon (kJ/kg), W is the mass of hydrocarbon (kg), W_{TNT} is the equivalent mass of TNT (kg) and α the yield factor.

Brasie and Simpson noted that the values quoted for the energy of explosion of TNT varied between 1800 BTU/lb (4190 kJ/kg) and 2000 BTU/lb (4650 kJ/kg), and adopted the latter.

From analysis of three vapour cloud explosion incidents they obtained values of the yield factor of 0.03–0.04, and on this basis proposed for use tentative values, intended to be conservative, of 0.02 in the near field and 0.05 in the far field, taken as that where the peak overpressure is 1 psi or less.

Brasie and Simpson also gave a graph and a table of damage versus peak overpressure, and made proposals for damage estimation.

17.28.11 TNT equivalent models: ACMH model

The *Second Report* of the ACMH (Harvey, 1979b) discusses the problem of vapour cloud explosions. In particular, it gives an equation for the cloud size, a suggested value for the explosion efficiency and an overpressure curve based on the TNT equivalent model. This information taken as a whole may be regarded as a form of model.

The relation for cloud size was quoted as Equation 15.46.47, and the suggested value of the yield was given as 0.03, as described in Section 17.27.7. The curve for peak overpressure is reproduced in Figure 17.73. The curve utilizes a damage classification based on bomb damage to dwelling houses in the Second World War. The classes given in the report as most relevant are:

Damage classification	*Damage*
A	Almost complete demolition
B	So severe as to necessitate demolition
Cb	House uninhabitable but not totally irreparable

'Glass damage' is expressed as the percentage of windows broken.

17.28.12 TNT equivalent models: Harris and Wickens model

The experimental work of R.J. Harris and Wickens (1989) has been described in Section 17.28.3. These authors also present a model of the TNT equivalent type.

In the Harris and Wickens model, the mass of gas participating in the vapour cloud explosion is restricted to the confined and congested part of the plant, and that

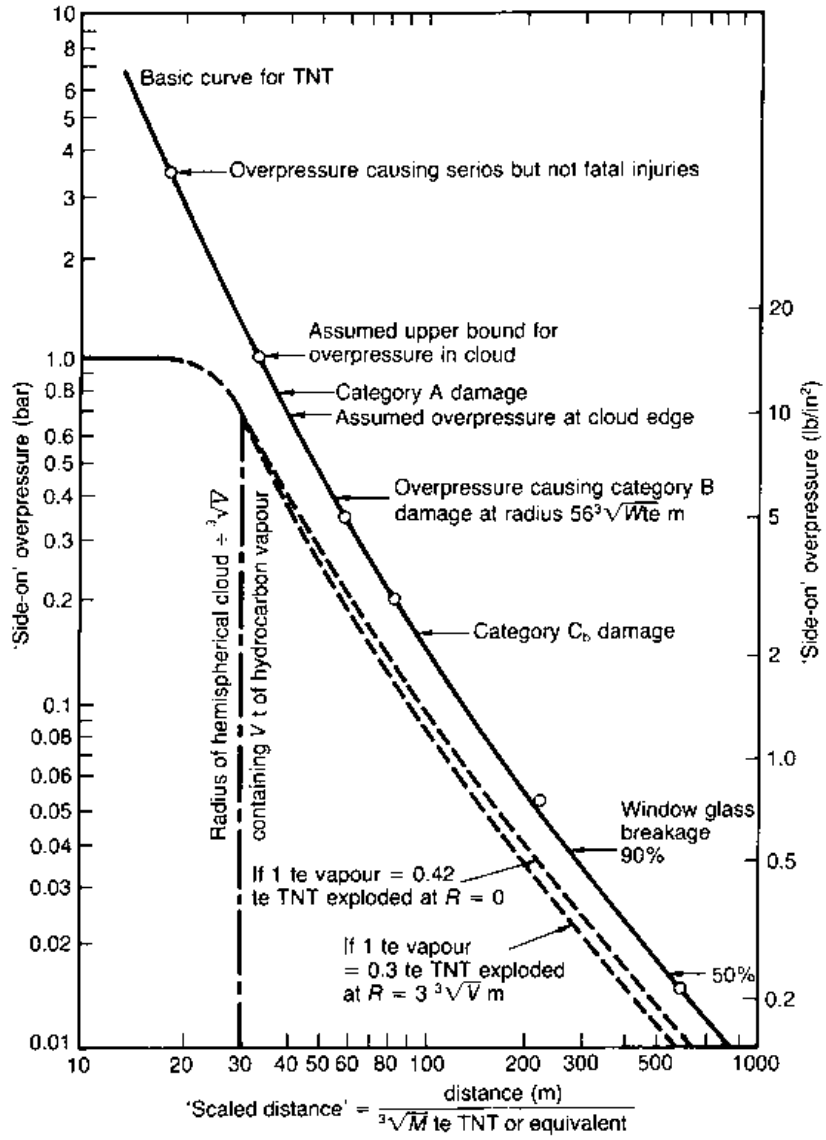


Figure 17.73 *Peak side-on overpressure for a vapour cloud explosion: ACMH correlation (Harvey, 1979b) (Reproduced by permission of HM Stationery Office. Copyright. All rights reserved.)*

in the unconfined part of the cloud is neglected. The yield on this more limited mass is taken as 0.20. The energy of explosion of TNT is taken as 4.6 MJ/kg and the heat of combustion of the hydrocarbon as 46 MJ/kg, a difference of a factor of 10. Then from the relation

$$M_{\mathrm{TNT}} = \alpha \frac{M_{\mathrm{gas}} E_{\mathrm{gas}}}{E_{\mathrm{TNT}}} \qquad [17.28.7]$$

the authors obtain

$$M_{\mathrm{TNT}} = 2M_{\mathrm{gas}} \qquad [17.28.8]$$

where E_{gas} is the heat of combustion of the hydrocarbon (MJ/kg), E_{TNT} is the energy of explosion of TNT (MJ/kg), M_{gas} is the mass of gas (in the confined/congested region) (te), M_{TNT} is the mass of TNT (te) and α is the yield factor. Equation (17.28.8) is obtained from Equation 17.28.7 with $E_{\mathrm{gas}}/E_{\mathrm{TNT}} = 10$ and $\alpha = 0.20$. Then taking for the density for the hydrocarbon–air mixture a value of 0.08 kg/m^3, yields from Equation 17.28.8

$$M_{\mathrm{TNT}} = 16 \times 10^{-5} V \qquad [17.28.9]$$

where V is the volume of gas (in the confined/congested region) (m^3).

The blast correlation used is that of the ACMH as given in Figure 17.73 (TNT curve).

As already described, these authors obtained for the peak overpressure at the edge of the vapour cloud a value of 4 bar, rather than the value of 1 bar proposed by the ACMH. They take this finding into account by determining the scaled distance for an overpressure of 4 bar on the ACMH graph, which is 16 $(m/te^{\frac{1}{3}})$ and proposing the use of an effective scaled distance of

$$16 + \frac{R}{(M_{TNT})^{\frac{1}{3}}} \qquad [17.28.10]$$

where R is the actual distance (m). This is effectively a virtual source correction.

17.28.13 TNT equivalent models: other models

In addition to those just described, several other TNT equivalent models for vapour cloud explosions have been developed, published or unpublished. They include those of Exxon (n.d.), Eichler and Napadensky (1977), Prugh (1987a), the FMRC (1990) and IRI (1990). These are reviewed by the CCPS (1994/15).

As already indicated, such models tend to differ in the methods used for (1) the mass of vapour participating in the explosion and (2) the yield factor of the explosion. Other differences relate to (3) the value used for the energy of explosion of TNT and (4) the correlation used for the peak overpressure of TNT.

Several of these models include a procedure for estimating the mass of flammable vapour which participates in the explosion. This aspect of the models is considered in Chapter 15.

The other main distinguishing feature of the models is in the estimation of the yield factor. This is considered in the next section.

The CCPS states that values used for the explosion energy of TNT lie in the range 4140–4650 kJ/kg, the same as that considered by Brasie and Simpson.

The blast correlations used in the models are given in Section 17.28.15.

The methods described are coherent procedures considered by their authors to give reasonable results. It is not appropriate to abstract particular features and use them indiscriminately. Each model is a 'package deal'.

It should also be borne in mind that models are developed for different purposes. The majority are essentially guides to the plant designer, particularly in relation to plant layout and control room design. Care should be exercised in applying such a model to hazard assessment or incident investigation.

17.28.14 TNT equivalent models: yield factor

The values used in the models mentioned for the yield factor are

Method	*Scenario/comment*	*Yield factor*
Brasie and Simpson	Near field	0.02
	Far field	0.05
ACMH		0.03
Exxon	Open terrain	0.03
	Partially confined and obstructed terrain	0.10
Eichler and Napadensky		0.20–0.40
Prugh	Mass of vapour cloud = 100 kg	0.02
	Mass of vapour cloud = 10^6 kg	0.70
Harris and Wickens	Mass in obstructed region only	0.20
FMRC	Relatively non-reactive material	0.05
	Moderately reactive material	0.10
	Highly reactive material	0.15
IRI		0.02

The model of Eichler and Napadensky is for safe separation distances between nuclear power plants and transport routes and refers to the far field (peak overpressure 1 psi (0.07 bar) and is evidently conservative. The higher of the two values given by Prugh refers to a very large cloud.

17.28.15 TNT equivalent models: blast correlation

The graphical correlations used for the peak overpressure from a TNT explosion are principally the following: Glasstone (1962) (Brasie and Simpson) and Glasstone and Dolan (1980) (IRI); V.C. Marshall (1976c) (ACMH); ACMH (Harris and Wickens); Kingery and Panill surface bursts (1964) (Exxon); and the US Army, Navy and Air Force (1990) (the *Tri-Service Manual*) (FMRC).

The ACMH correlation is based on that of V.C. Marshall (1976c). This has been reproduced in the literature with different scaled distances. In the ACMH graph the mass used in the scaled distance is in tonnes, in the graph given by the CCPS (1994/15) the mass is explicitly stated to be in kilograms.

17.28.16 TNT equivalent models: yield ratio

For completeness in the treatment of the TNT equivalent model, it is convenient to deal at this point with the question of the yield ratio, or symmetry factor.

As explained earlier, if a free air burst correlation is used for the blast parameters, but the application is to a ground burst, an appropriate yield ratio is applied to the actual energy of explosion, or equivalent mass of TNT, to obtain an effective energy, or mass, for use in calculation of the scaled distance.

The simple, and conservative, approach is to take this yield ratio as 2.

The value of the yield ratio is discussed by the CCPS (1994/15). It suggests that the value of the yield ratio will generally lie in the range 1.7–2. The lower value may preferred if the epicentre of the explosion is slightly above the ground.

17.28.17 Taylor model

An early model of a vapour cloud explosion was given in a classic paper by G.I. Taylor (1946). He considers small pressure disturbances, as in acoustics, so that the system

equations can be linearized. The treatment which he describes is in terms of an expanding piston for which from the conservation equations in spherical geometry he obtains the wave equation

$$r^2 \frac{\partial^2 \phi}{\partial t^2} = a_o^2 \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) \right] \quad [17.28.11]$$

with the velocity potential ϕ such that

$$u = \frac{\partial \phi}{\partial r} \quad [17.28.12]$$

$$p - p_o = -\rho_o \frac{\partial \phi}{\partial t} \quad [17.28.13]$$

where a_o is the speed of sound, p is the absolute pressure, p_o is the ambient pressure, r is the radial distance, t is the time, u is the velocity and ρ_o is the density of the ambient gas, and ϕ is the velocity potential. The term $(p-p_o)$ is thus the overpressure.

The boundary condition used is such that the velocity of the medium is equal to that of the piston. From this Taylor obtains the velocity potential as

$$\phi = a_o \frac{M_p^3}{1 - M_p^2} \frac{(r - a_o t)^2}{r} \quad [17.28.14]$$

and hence

$$\bar{p} = 2\gamma \frac{M_p^3}{1 - M_p^2} \left(\frac{a_o}{r} - 1 \right) \quad [17.28.15]$$

with

$$\bar{p} = \frac{p - p_o}{p_o} \quad [17.28.16]$$

where M_p is the Mach number of the piston, $\bar{p}$ is the dimensionless overpressure and γ is the ratio of the specific heats.

Equating the mass within the piston flow field and that within the flame flow field yields the following relation between the piston and flame Mach numbers:

$$M_p^3 = M_f^3 \left(\frac{\alpha - 1}{\alpha} \right) \quad [17.28.17]$$

where M_f is the flame Mach number and α is the expansion ratio.

17.28.18 Strehlow model

The vapour cloud explosion model given by Strehlow (1981) also follows the acoustic approach, but utilizes a constant velocity piston.

It was shown by Stokes (1849) that a source of mass with mass flow $\dot{m}(t)$ generates a sound wave in three dimensions which has an overpressure that is proportional to $\ddot{m}(t)$. Lighthill (1978) gave this concept the specific formulation

$$p - p_o = \frac{\ddot{m}}{4\pi r} (t - r/a_o) \quad [17.28.18]$$

where a_o is the velocity of sound, p is the absolute overpressure, p_o is the ambient pressure and r is the characteristic radius of the source region. Here time t is replaced by the term $(t - r/a_o)$ because the wave is propagating away from the source at the velocity of sound.

Then for deflagrative combustion the effective rate of volume addition $\dot{V}(t)$ is related to that of mass addition $\dot{m}(t)$:

$$\dot{m}(t) = \rho_o \dot{V}(t) \quad [17.28.19]$$

where ρ_o is the initial density of the gas.

The rate of volume addition can also be expressed in terms of the rate of change of the flame surface. Hence

$$\dot{m}(t) = \rho_o \left(\frac{V_b - V_u}{V_u} \frac{d}{dt} [S_u(t) A_f(t)] \right) \quad [17.28.20]$$

where A_f is the effective frontal area of the flame, S_u is the burning velocity, V_b is the specific volume of the burned gas and the V_u the specific volume of the unburned gas.

Then from the expression for the velocity of sound in an ideal gas and from Equations 17.28.18 and 17.28.20

$$\bar{p} = \frac{\hat{q}}{4\pi r a_o^2 r} \frac{d[S_u(t) A_f(t)]}{dt} \quad [17.28.21]$$

with

$$\hat{q} = \gamma \frac{V_b - V_u}{V_u} \quad [17.28.22]$$

where $\bar{p}$ is the dimensionless overpressure, $\hat{q}$ is the dimensionless rate of energy addition and γ is the ratio of specific heats.

For a constant velocity flame, Equation 17.28.27 reduces to

$$\bar{p} = \frac{\hat{q}}{4\pi r a_o^2 r} S_u \frac{dA_f(t)}{dt} \quad [17.28.23]$$

Then for spherical geometry, utilizing in Equation 17.28.23 the relations

$$A_f = 4\pi r_f^2 \quad [17.28.24]$$

$$\frac{dr_f}{dt} = S_b \quad [17.28.25]$$

$$S_b = S_u \frac{V_b}{V_u} \quad [17.28.26]$$

and the definition of $\hat{q}$, applying the constant velocity flame relation $r_f = S_b t$ and substituting for t the term $(t - r/a_o)$, yields

$$\bar{p} = 2\gamma \left(1 - \frac{V_u}{V_b} \right) \left(\frac{V_b}{V_u} \right)^3 M_{su}^3 \left(\frac{a_o t}{r} - 1 \right) \quad [17.28.27]$$

where M_{su} is the Mach number in the unburned gas.

The relation between this model and that of Taylor at low flames speeds may be demonstrated as follows. Using Taylor's relation between the flame and piston Mach numbers, Equation 17.28.17, and the relations

$$\alpha = V_b / V_u \quad [17.28.29]$$

$$\frac{dr_f}{dt} = u_f \quad [17.28.30]$$

$$M_f = M_{su} \frac{V_b}{V_u} \quad [17.28.30]$$

where u_f is the velocity of the flame front. It can be shown that for low values of the flame Mach number M_f, Equation 17.28.27 is equivalent to Equation 17.28.15.

Equation (17.28.23) is a general relation which may be applied to vapour clouds of different geometries. The different cases may be examined by substituting different expressions for A_f and hence dA_f/dt. For spherical geometry utilizing for A_f Equation 17.28.24 gives

$$\bar{p} = \frac{2\hat{q}S_u^2 r_f}{ra_o^2}\frac{V_b}{V_u} \qquad r \geq r_f \qquad [17.28.31]$$

Using alternative expressions for the flame area A_f and the rate of change of the flame radius dr_f/dt, Strehlow obtains expressions for the overpressure in explosions of vapour clouds of other geometries and other points of ignition. These include an ellipsoid, a cigar-shaped cloud with end point ignition, and pancake clouds with centre and with edge ignition.

Thus for a pancake cloud

$$A_f = 2\pi r_f H \qquad [17.28.32]$$

where H is the height of the cloud. Then

$$\bar{p} = \frac{\hat{q}S_u^2 H}{2a_o^2 r_{obs}}\frac{V_b}{V_u} \qquad [17.28.33]$$

where r_{obs} is the distance of the observer from the centre of the cloud.

Strehlow also obtains an order of magnitude estimate of the effect of cloud size. For an overpressure of 0.1 bar at a distance 100 m from the cloud centre and with a velocity of sound of 350 m/s Equation 17.28.21 reduces to

$$A_f\frac{dS_u}{dt} + S_u\frac{dA_f}{dt} = 1.6 \times 10^7\ m^3/s^2 \qquad [17.28.34]$$

Then the use of the alternative limiting assumptions $dS_u/dt = 0$ and $dA_f/dt = 0$ allows values of dA_f/dt and dS_u/dt, respectively to be calculated. Table 17.35 shows the values given by Strehlow. The table shows that even for a very high flame velocity the rate of increase of flame area must also be very high to generate even a weak blast wave, while only a very large flame area, with a very large acceleration, is able to produce a weak blast wave. He concludes that for a significant overpressure to be generated by deflagrative combustion alone a very large cloud is required.

Further development of this approach for clouds of different aspect ratios has been described by Raju and Strehlow (1984).

Table 17.35 *Strehlow model for vapour cloud explosion: effect of burning velocity and flame area (after Strehlow, 1981) (Courtesy of the American Institute of Chemical Engineers)*

A $dS_u/dt = 0$

S_u	dA_f/dt
m/s	m^2/s
1	1.7×10^7
10	1.7×10^6
100	1.7×10^5

B $dA_f/dt = 0$

A_f	dS_u/dt
(m^2)	(m/s^2)
10^2	1.7×10^5
10^4	1.7×10^3
10^6	17

17.28.19 Model of Kuhl, Kamel and Oppenheim

In another classic paper, Kuhl, Kamel and Oppenheim (1973) presented an 'exact' similarity solution for the conservation equations which they give in the form

$$\frac{F}{2Z}\frac{dF}{dZ} = \frac{Z - (1-F)^2 + (\gamma-1)(1-F)F}{3Z - (1-F)^2} \qquad [17.28.35]$$

$$\frac{F}{X}\frac{dX}{dF} = \frac{-Z + (1-F)^2}{3Z - (1-F)^2} \qquad [17.28.36]$$

with

$$F = \frac{u}{U_s X} \qquad [17.28.37]$$

$$Z = \left(\frac{a}{U_s X}\right)^2 \qquad [17.28.38]$$

$$X = \frac{r}{r_s} \qquad [17.28.39]$$

where a is the speed of sound, r is the radial distance, r_s is the radial distance of the leading shock, u is the particle velocity and U_s is the velocity of the leading shock.

Their model is based on a constant velocity piston. The leading shock travels ahead of the piston with the flame front in between.

In the form given, the model has to be solved numerically.

The authors explored the implication of their model for flame speeds ranging from 0.5 to 120 m/s. The maximum overpressure ratio obtained was 6, with flame speeds of 5–10 m/s being associated with overpressure ratios of the order of 0.05–0.10. They give a set of curves showing the strong increase of overpressure with flame speed.

17.28.20 Williams model

A number of workers have obtained approximate analytical solutions of the constant velocity piston case based on self-similarity. The model of F.A. Williams (1976), also discussed by Anthony (1977a), is illustrative of this approach.

In the model it is assumed that ignition occurs at a point source, that the flame front which develops travels out from the 'core' at a flame speed S and that the pressure waves produced by the flame generate a weak shock which travels ahead of the flame at a velocity $V(t)$ which varies with time. It is also assumed that the pressure and density in the 'shell' between the flame and shock fronts are constant.

Then for spherical symmetry the model equation for conservation of momentum across the shock wave is

$$p_1 - p_o = \rho_o \left(\frac{dR}{dt}\right)^2 \left(1 - \frac{\rho_o}{\rho_1}\right) \quad [17.28.40]$$

or in dimensionless form

$$p = 1 + (1 - K)\left(\frac{dy}{d\tau}\right)^2 \quad [17.28.41]$$

The other basic equations, also in dimensionless form, are for conservation of mass for a sphere of radius R,

$$\theta p x^3 + \frac{(y^3 - x^3)}{K} = y^3 \quad [17.28.42]$$

and for conservation of mass for the burned core,

$$\frac{x^2 s}{K} = \frac{d}{d\tau}(\theta p x^3/3) \quad [17.28.43]$$

The similarity solution is

$$s = \frac{Kq\theta p(p-1)^{\frac{1}{2}}}{(1 - K\theta p)^{\frac{1}{3}}(1-K)^{\frac{1}{6}}} \quad [17.28.44]$$

with

$$p = p_1/p_o \quad [17.28.45a]$$

$$s = S/a_o \quad [17.28.45b]$$

$$x = r/R_o \quad [17.28.46a]$$

$$y = R/R_o \quad [17.28.46b]$$

$$\theta = T_o/T_2 \quad [17.28.47a]$$

$$K = r_o/r_1 \quad [17.28.47b]$$

$$\tau = a_o t/R_o \quad [17.28.47c]$$

where a_o is the speed of sound $(=(p_o/\rho_o)^{\frac{1}{2}})$, p_i is the absolute pressure in region i, r is the flame radius, R is the shock radius, R_o is the initial value of the shock radius, S is the flame speed, t is the time, T_i is the absolute temperature in region i, ρ_i is the gas density in region i and τ is the dimensionless time. The subscripts o, 1, 2 of p, T and ρ refer, respectively, to conditions in the undisturbed gas, the shocked gas (shell) and the burnt gas (core). The variables K, θ and p are time dependent.

The model yields a number of interesting results. One is that from Equation 17.28.40 the shock wave pressure has a well defined upper limit. Another is that for transition to detonation the flame speed must be an appreciable fraction of the speed of sound:

$$s > (K/3)[(p-1)(1-K)]^{\frac{1}{2}} \quad [17.28.48]$$

17.28.21 Other similarity models

The model just described is one a number of approximate analytical models.

A review of this work is given by the CCPS (1994/15), which presents for some of the models a set of graphs of the flow field parameters, in each of which the curves of particular workers are compared with those of the 'exact' solution.

17.28.22 Gugan model

In his review of vapour cloud explosions, Gugan (1979) includes a model based on self-similarity which he uses to examine the characteristics of such explosions. This model is not in the mainstream of vapour cloud explosion models, but constitutes an interesting approach, particularly to behaviour in the near field.

The blast wave from a vapour cloud explosion is inherently unstable, and at a point quite close to the centre of the explosion it transforms into a shock wave. Beyond this transformation point, in the far field, no distinction can be made between a condensed phase explosion or a vapour cloud explosion on the basis of the shock wave. But between the explosion centre and the transformation point, in the near field, some interesting features emerge.

Gugan uses the following relation for the pressure profile:

$$p = \frac{\dot{p}_c t}{2}\left[1 + \cos\left(\frac{\pi r}{at}\right)\right] \qquad 0 < r \le at \quad [17.28.49]$$

where a is the velocity of sound in the normal atmosphere, p is the pressure, p_c is the pressure at the centre of the explosion, r is the distance from the centre of the blast symmetry and t is the time. The term $\dot{p}_c t$ is therefore the pressure at the centre of the explosion. The form of curve given by this equation is the 'companion to the cycloid'.

Utilizing the relations for the energy E contained in the compressed gases $E = \int V\,dp$ and for the relation between the pressure p and the volume V for an isentropic expansion $\int V\,dp = {}^{-}\gamma \int p\,dV$ (where γ is the ratio of the gas specific heats) together with Equation 17.28.49, Gugan obtains for the pressure at the centre of the explosion

$$\dot{p}_c t = \frac{E_o}{0.57(at_o)^3} \quad [17.28.50]$$

where E_o is the total energy release and t_o is the time of termination of the rapid energy release. Equation 17.28.50, and alternative relations derived by the author, provide the value of the term $\dot{p}_c t$ in Equation 17.28.49 and allow estimates to be made of the pressure profile.

The author compares the relation which he derives for the pressure profile from a vapour cloud explosion with that from a condensed phase explosion. These relations indicate that for the same energies and distances, the amplitude of the shock wave from a condensed phase explosion exceeds that from a vapour cloud explosion by one or two orders of magnitude. Yet the shock waves from vapour cloud explosions are very destructive. He concludes that this is due to the longer duration time of the positive phase in vapour cloud explosions and suggests that the factor of two, which is sometimes given for the ratio of the duration time in a vapour cloud explosion to that in a condensed phase explosion, is probably an underestimate.

Gugan defines an explosion efficiency η:

$$\eta = E_e/E_u \quad [17.28.51]$$

where E_e is the explosive energy release, E_u is the vapour cloud energy release. For the latter

$$E_u = m\,\Delta H_c \quad [17.28.52]$$

where ΔH_c is the heat of combustion and m is the mass of fuel in the cloud. He obtains for the explosion efficiency expressions of the general form

$$\eta = \frac{f(m;\ \Delta H_c;\ M;\ \epsilon;\ \nu)}{f(R)} \qquad [17.28.53]$$

where M is the molecular weight of the vapour, ϵ is the stoichiometric ratio and ν is the flame speed.

The expression for the explosion efficiency shows the efficiency as a function of various characteristics of the fuel. In the near field it falls off rapidly with distance R, being inversely proportional to R^3.

This model proved controversial and was criticized by Ale and Bruning (1980). One feature is the decay of efficiency, which did not appear to sit well with the effects of actual explosions. A review has been given by H. Phillips (1981b).

17.28.23 Baker–Strehlow model

Strehlow, Luckritz and co-workers conducted numerical studies, using the CLOUD code, exploring for spherical geometry the characteristics of flames travelling at constant velocity and with acceleration (Luckritz, 1977; Strehlow *et al.*, 1979) and obtained relationships for the blast wave parameters. This work was extended by W.E. Baker *et al.* (1983) to yield the Baker–Strehlow method for vapour cloud explosions.

The scaled peak overpressure and the scaled impulse given by this method are shown in Figures 17.74 and 17.75, respectively. The scaled variables are given by Equations 17.26.7–17.26.9. The graphs are for spherical symmetry.

Figure 17.74 utilizes two Mach numbers, M_w, which relates to fixed co-ordinates, and M_{su}, which is relative to the gases moving ahead of the flame front. The relationship between these two Mach numbers is discussed by Strehlow *et al.* (1979). At high Mach numbers $M_{su} \rightarrow M_w$. The solid lines in the figure represent numerical calculations, and the broken lines extensions of Taylor's model to the very low Mach number range. Also shown in the figure are curves for pentolite, for a bursting sphere and for detonation (CJ curve).

The method requires values of the energy of explosion and the flame speed. The explosion energy may be determined using one of the methods described in Section 17.28.14 in relation to the TNT equivalent model. The flame speed is estimated by considering the effect of the combination of factors known to influence it: the reactivity of the fuel, the strength of the ignition source and the degree of confinement and congestion.

17.28.24 Wiekema model (TNO shock wave model)

Three models of vapour cloud explosion have been developed by TNO. The first of these is the shock wave model described in the *Yellow Book* and by Wiekema (1980). The model is also known as the expanding piston or piston blast model. It allows the peak overpressure and the duration time of the explosion to be estimated.

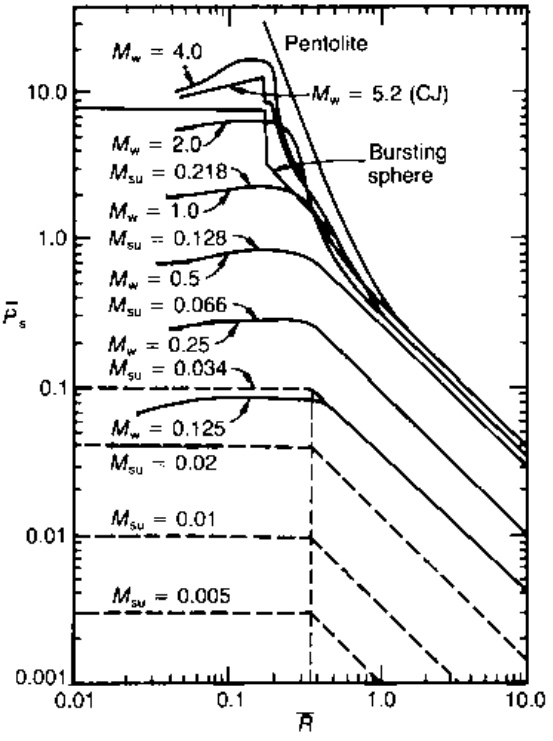


Figure 17.74 *Scaled peak side-on overpressure for a vapour cloud explosion (Strehlow et al., 1979). Curves and Mach numbers are explained in the text (Courtesy of the Combustion Institute)*

The model is a composite one derived from separate models for deflagration and detonation in the cloud. Considering first the model for deflagration, it has been shown by Strehlow, Savage and Vance (1973) that given the pressure–time profile it is possible to derive the energy of an explosion. Wiekema uses this result, inverting it to obtain the pressure–time profile from an arbitrary energy release.

The cloud is assumed to be a hemisphere of unburnt gas volume V_o which expands during the combustion process to a hemisphere volume V_1. In this process the energy added to the unburnt gas is assumed to be added by a hemispherical piston, this process effectively replacing the combustion process. This energy E_o is

$$E_o = \int_o^\infty p \frac{dV}{dt} dt \qquad [17.28.54a]$$

$$\approx p_o(V_1 - V_o) \qquad [17.28.54b]$$

$$= n_1 R_g T_1 - n_o R_g T_o \qquad [17.28.54c]$$

$$= p_o V_o \frac{n_1 T_1}{n_o T_o} - 1 \qquad [17.28.54d]$$

where E_o is the total energy of the explosion (J), n is the number of moles, p is the absolute pressure (Pa), R_g is

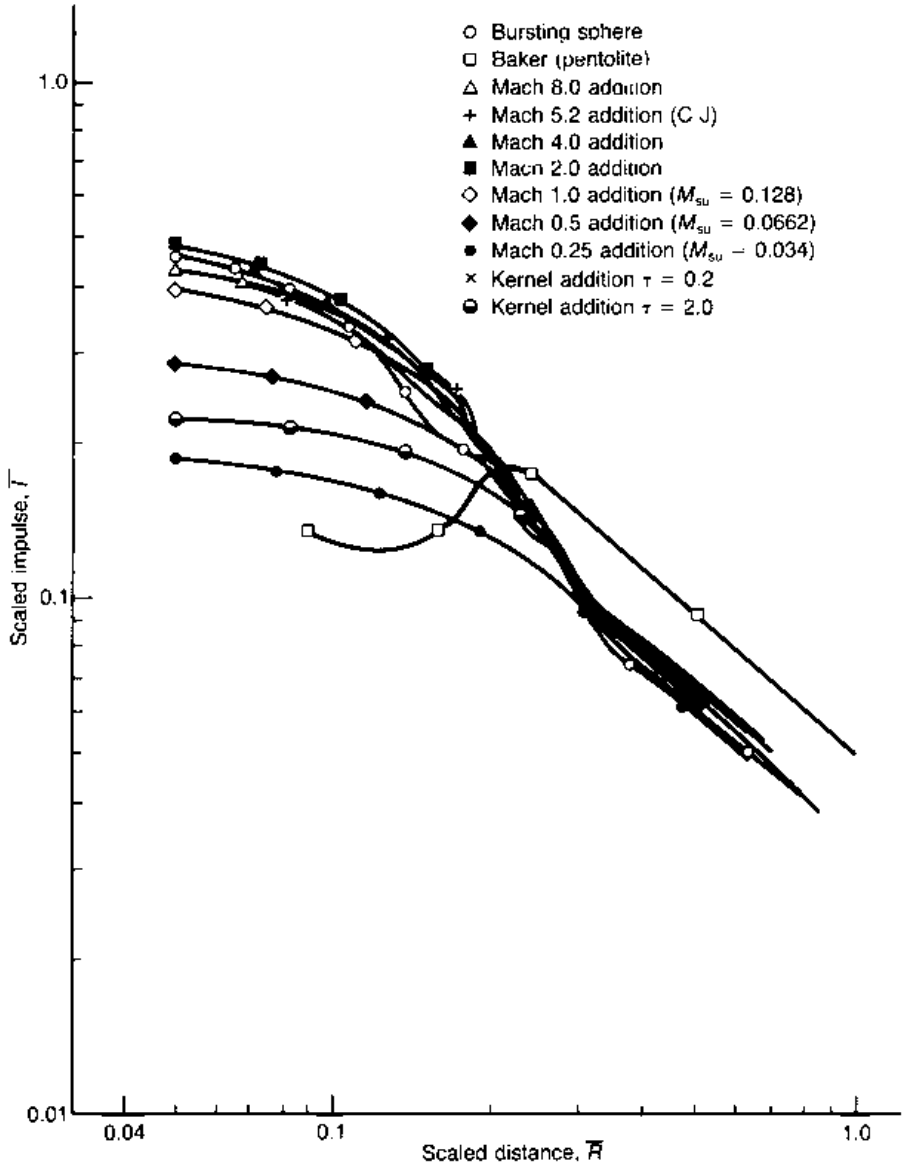


Figure 17.75 *Scaled side-on impulse for a vapour cloud explosion (Strehlow et al., 1979) (Courtesy of the Combustion Institute)*

the universal gas constant (J/mol K), T is the absolute temperature (K), V is the volume (m^3) and the subscripts o and 1 denote initial and final conditions, respectively.

But

$$E_o = \frac{2}{3}\pi R_o^3 E_c \qquad [17.28.55]$$

where E_c is the energy of combustion per unit volume (J/m^3) and R_o is the radius of the initial cloud (m).

A characteristic explosion length L is defined as

$$L = \left(\frac{E_o}{p_o}\right)^{\frac{1}{3}} \qquad [17.28.56a]$$

$$= \left(\frac{2}{3}\pi R_o^3 \frac{E_c}{p_o}\right)^{\frac{1}{3}} \qquad [17.28.56b]$$

where L is the characteristic length (m), and a parameter λ as

$$\lambda = \frac{L}{t_b} \qquad [17.28.57]$$

where t_b is the time (s) at which the expansion process is complete. A reduced distance $\bar{R}$, reduced overpressure $\overline{PS}$, reduced time $\bar{t}$ and reduced duration time $\overline{TS}$ are then defined as follows:

$$\bar{R} = \frac{R}{L} \qquad [17.28.58]$$

$$\overline{PS} = \frac{p - p_o}{p_o} \qquad [17.28.59]$$

$$\bar{t} = \frac{t}{t_b} \qquad [17.28.60]$$

$$\overline{TS} = \frac{t + c_o}{L} \qquad [17.28.61]$$

where c_o is the local velocity of sound (m/s), R is the distance (m) and t_+ is the duration time (s).

The reduced overpressure is taken as inversely proportional to the reduced distance:

$$\overline{PS} = \frac{A}{\bar{R}} \qquad [17.28.62a]$$

$$= \frac{AL}{R} \qquad [17.28.62b]$$

where A is a constant.

From shock wave theory

$$U_{sw} = \frac{dR}{d\bar{R}} \qquad [17.28.63a]$$

$$= c_o\left(1 + \frac{\gamma + 1}{4\gamma}\overline{PS}\right) \qquad [17.28.63b]$$

where U_{sw} is the velocity of the shock wave (m/s) and γ the ratio of specific heats for air. Taking $\gamma = 1.4$,

$$\frac{dR}{dt} = c_o\left(1 + \frac{3}{7}\overline{PS}\right) \qquad [17.28.64a]$$

$$= c_o\left(1 + \frac{3AL}{7R}\right) \qquad [17.28.64b]$$

The duration time is determined as the difference between the arrival times of the shock wave and the sound wave and at the radius R_1 of the burnt cloud is

$$t_+ = R_1\left(\frac{1}{\bar{v}_{fl}} - \frac{1}{c_o}\right) \qquad [17.28.65]$$

where $\bar{v}_{fl}$ is the average flame speed (m/s).

The velocities of the shock wave and sound wave in the cloud and beyond are shown in Figure 17.76.

Integrating Equation 17.28.64b gives

$$t_+ = R_1\left(\frac{1}{\bar{v}_{fl}} - \frac{1}{c_o}\right) + \frac{3}{7}A\frac{L}{c_o}\ln\left(\frac{1 + 7R/3AL}{1 + 7R_1/3AL}\right) \qquad R > R_1 \qquad [17.28.66]$$

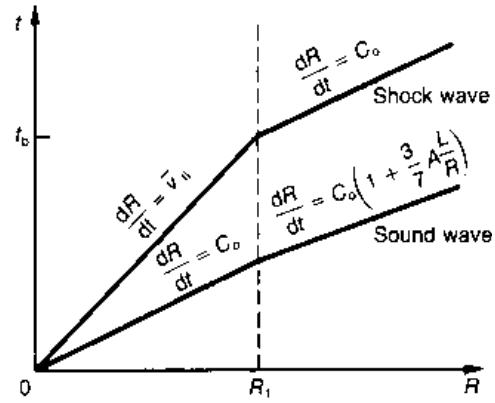


Figure 17.76 *TNO shock wave model for vapour cloud explosions: propagation of flame front and sound wave (Wiekema, 1980) (Courtesy of Elsevier Science Publishers)*

At the cloud boundary ($R = R_1$), Equation 17.28.66 reduces to Equation 17.28.65. The reduced duration time is then

$$\overline{TS} = \frac{R_1}{L}\left(\frac{c_o}{\bar{v}_{fl}} - 1\right) + \frac{3}{7}A\ln\left(\frac{1 + 7R/3AL}{1 + 7R_1/3AL}\right) \qquad R > R_1 \qquad [17.28.67]$$

In evaluating Equation 17.28.67 use is made of the relation $R_1/L = 0.456$ derived from the definitions given in the work.

The following numerical values are assumed in the work:

$$\frac{n_1 T_1}{n_o T_o} = 7$$

$$E_c = 3.5 \times 10^6\ \text{J/m}^3$$

The energy added per unit volume, which is the energy available for shock wave formation, is 6×10^5 and is thus some 17% of the available combustion energy, assuming a stoichiometric mixture. The velocity of sound c_o in air may be taken as 330 m/s.

The method involves selecting an assumed flame speed. The set of flame speeds $\bar{v}_{fl}$ quoted are 40, 80 and 160 m/s, and the corresponding values of the parameter A are 2×10^{-2}, 6×10^{-2} and 15×10^{-2}, respectively.

The reduced overpressure $\overline{PS}$ and reduced duration time $\overline{TS}$ are both functions of the reduced distance $\bar{R}$, as shown in Figure 17.77.

As an illustration of the method, consider the estimation of the peak overpressure and duration time at a distance R of 500 m for a vapour cloud explosion in a hemispherical cloud of initial radius R_o of 100 m assuming an average flame speed of 80 m/s. Then from Equation 17.28.56b

$$L = \left(\frac{2}{3}\pi(100)^3 + \frac{3.5 \times 10^6}{10^5}\right)^{\frac{1}{3}}$$

$$= 418\ \text{m}$$

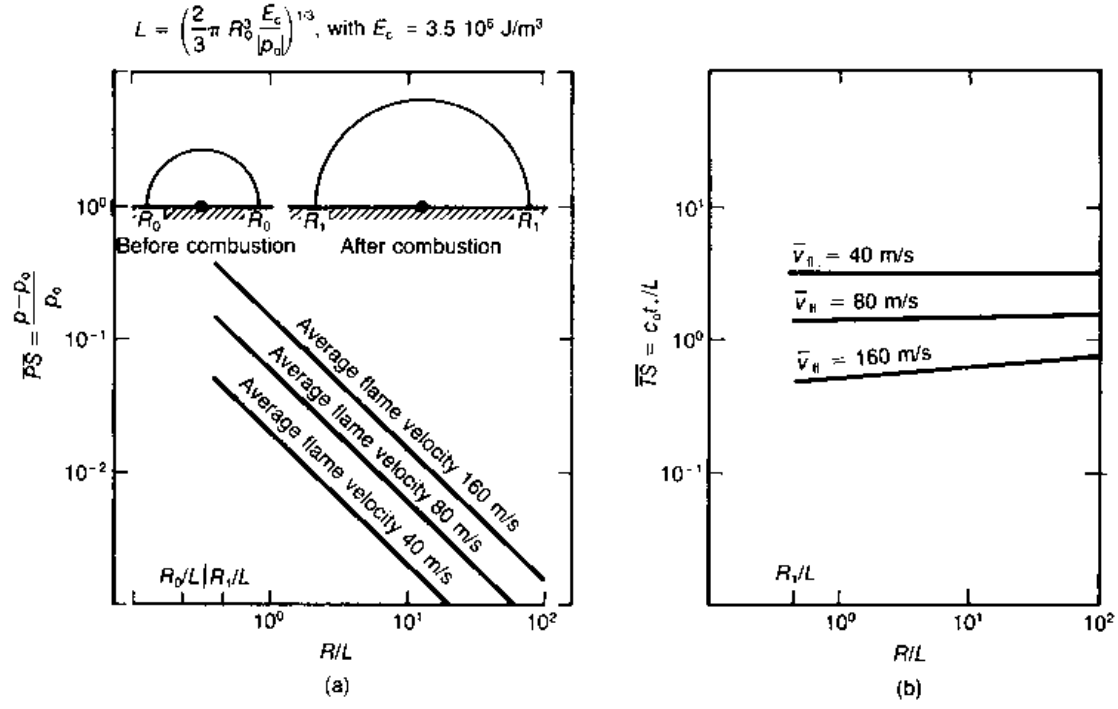


Figure 17.77 *TNO shock wave model for vapour cloud explosions – peak overpressure and duration of the blast wave, as a function of flame speed (Wiekema, 1980): (a) scaled peak overpressure; (b) scaled duration time (Courtesy of Elsevier Science Publishers)*

Hence

$R_1 = 0.456L$

$= 0.456 \times 418$

$= 191$ m

From Equation 17.28.58

$\bar{R} = 500/418$

$= 1.2$

From Equation 17.28.62, taking the value of A corresponding to the average flame speed v_{fl} of 80 m/s,

$\overline{PS} = 6 \times 10^{-2}/1.2$

$= 0.05$

Hence from Equation 17.28.59 the peak overpressure $(p - p_o)$ for an initial pressure p_o of 10^5 Pa (1 bar) is

$p - p_o = 0.05 \times 10^5$ Pa

$= 0.05$ bar

And from Equation 17.28.67

$$\overline{TS} = 0.456\left(\frac{330}{80} - 1\right) + \frac{3}{7} \times 6 \times 10^{-2} \times \ln\left(\frac{1 + (7 \times 1.2)/(3 \times 6 \times 10^{-2})}{1 + (7 \times 0.456)/(3 \times 6 \times 10^{-2})}\right)$$

$= 1.45$

Hence from Equation 17.28.61

$t_+ = 1.45 \times 418/330$

$= 1.83$ s

The model just described is applicable to a deflagration. For the case of detonation in a vapour cloud Wiekema utilizes results obtained by Kogarko, Adushkin and Lyamin (1966), from which he obtains the following relations for the reduced overpressure and reduced duration time:

$\overline{PS} = 0.518\bar{R}^{-1.7}$ $\quad 0.29 < \bar{R} < 1.088$ [17.28.68a]

$= 0.2177\bar{R}^{-1}$ $\quad \bar{R} > 1.088$ [17.28.68b]

$\overline{TS} = 0.1853\bar{R}^{\frac{1}{2}}$ $\quad 0.36 < \bar{R} < 12.6$ [17.28.69a]

$= 0.20 + 0.0933 \ln(1 + 10.7\bar{R})$ $\quad \bar{R} > 12.6$ [17.28.69b]

Since in the detonation work no results are given for $\overline{TS}$ for $\bar{R}>12.6$, Equation 17.28.69b is based on the deflagration work.

Wiekema then consolidates these two models, for deflagration and detonation in a vapour cloud, into a single vapour cloud explosion model. The reduced overpressure $\overline{PS}$ and reduced duration time $\overline{TS}$ are shown as functions of the reduced distance $\bar{R}$ in Figure 17.78.

The lines shown in Figure 17.78 are the boundaries of materials of low, medium and high reactivity. Reactivity is essentially sensitivity to flame acceleration. For each class the lower boundary is used unless there is reason to expect a relatively high flame acceleration.

The reduced overpressure $\overline{PS}$ is again inversely proportional to reduced distance $\bar{R}$, except at the upper boundary for high reactivity materials.

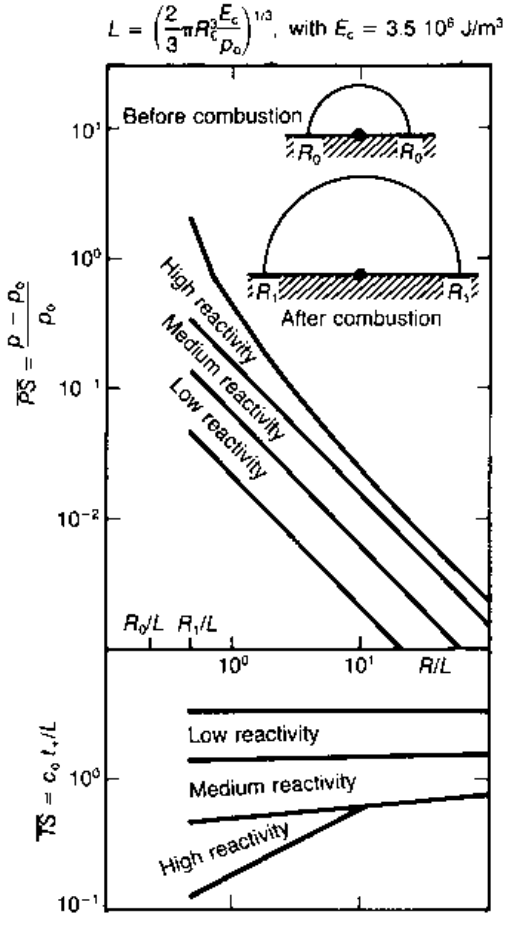


Figure 17.78 *TNO shock wave model for vapour cloud explosions – peak overpressure and duration of the blast wave, as a function of fuel reactivity (Wiekema, 1980): (a) scaled peak overpressure and (b) scaled duration time (Courtesy of Elsevier Science Publishers)*

Wiekema states that methane is considered as a fuel of low reactivity, ethane and butane as fuels of medium reactivity and hydrogen, ethylene oxide and acetylene as fuels of high reactivity.

17.28.25 TNO correlation model

The second TNO vapour cloud explosion model is the correlation model; this too is described in the *Yellow Book*. The model allows an estimate to be made of the radius of defined damage circles. It does not give explosion parameters such peak overpressure or duration time.

The model is based on a correlation for vapour cloud explosion incidents of damage effects outside the gas cloud.

The correlation is based on the energy content E of the part of the cloud within the explosive range. This energy is

$$E = M_e \, \Delta H_c \qquad [17.28.70]$$

where E is the energy content of the part of the cloud within the flammable range (J), M_e is the mass of fuel in the cloud within the flammable range (kg) and ΔH_c is the heat of combustion (J/kg).

If the energy content $E < 5 \times 10^9$, corresponding to approximately 100 kg of hydrocarbon, the cloud is so small that no serious damage would be anticipated, while if $E > 5 \times 10^{12}$ the cloud is so large that no data are available on which to base a correlation. The model is applicable only to clouds with an energy content within those bounds.

The energy actually released is only a fraction η of the energy content E. This fraction, or efficiency, is the product of two separate efficiencies:

$$\eta = \eta_c \eta_m \qquad [17.28.71]$$

where η_c is a yield factor which takes account of the fact that the flammable part of the cloud is not a stoichiometric mixture and η_m is another yield factor which gives the mechanical energy yield of the combustion. The factor η_m is given different values, depending on whether combustion is at constant pressure or constant volume:

Constant pressure combustion $\eta_m = 0.18$

Constant volume combustion $\eta_m = 0.33$

Since in combustion of a vapour cloud explosion tends to be associated with a degree of confinement, the constant volume value of η_m (= 0.33) is recommended.

The relation for the radius of the damage circles is

$$R(S) = C(S)(\eta E)^{\frac{1}{3}} \qquad [17.28.72]$$

where $C(S)$ is a constant which is a function of the degree of damage S (m/J$^{\frac{1}{3}}$), E is the energy content (J), $R(s)$ is the radius of the damage circle (m) and η is the explosion efficiency.

The values of the constant $C(S)$ are as follows:

Damage	$C(S)$ $(m/J^{\frac{1}{3}})$
Heavy damage to buildings and to processing equipment	0.03
Repairable damage to buildings and facade damage to dwellings	0.06
Glass damage causing injury	0.15
Glass damage ($\approx$ 10% of panes)	0.4

17.28.26 van den Berg model (TNO multi-energy model)

The third TNO vapour cloud explosion model is the multi-energy (ME) model described by van den Berg (1985). This model allows the peak overpressure, peak dynamic pressure and duration time to be estimated.

The starting point for this model is recognition of the role of partial confinement in vapour cloud explosions. It is assumed in the model that the explosion in those parts of the cloud which are confined is of much higher strength than in those where it is unconfined. The method involves estimating the combustion energy available in the various parts of the cloud and assigning to each part an initial strength.

This initial strength is denoted by a number in the range 1–10, where 1 applies to an explosion of insignificant strength and 10 to a detonation. Confined parts of the cloud are usually assigned a strength greater than 6 or 7.

The peak overpressure, peak dynamic pressure and duration time are estimated using Figure 17.79. For a given part of the cloud the energy of explosion in that part is determined, an initial strength is estimated and the blast parameters are then calculated.

The simplest case is that of a cloud with a single high strength source of reasonable size. The situation is more complex if this high strength source is small or if there are multiple high strength sources. Some judgement is required, therefore, in applying the method.

Van den Berg gives as an illustration of the method the estimation of the peak overpressure and duration time of the vapour cloud explosion at Flixborough.

17.28.27 Numerical modelling

An alternative approach to the modelling of vapour cloud explosions is the use of computational fluid dynamics (CFD) codes. An account of their application is given by the CCPS (1994/15).

The CFD modelling of vapour cloud explosions is not entirely straightforward. There is a difficulty due to discontinuities, both contact discontinuity between the burned and unburned gases and shock discontinuity. For a blast flow field conventional numerical methods tend to yield inaccurate results.

In order to overcome these problems researchers have resorted to two devices. One is the use of artificial viscosity and the other the use of flux-corrected transport (FCT). The former was introduced by von Neumann and Richtmyer (1950) and the latter is described by Boris (1976) and Boris and Book (1976).

Both Eulerian and Langrangean formulations are used. The difference between these in their application to gas dispersion is touched on in Chapter 15 and is discussed in standard texts (e.g. Meteorological Office, 1972).

Many workers have used the artificial viscosity method with the gas dynamics in Lagrangean form. They include Fishburn (1976), van den Berg (1984) and van Wingerden (1984 CEC EUR 9541 EN/II).

The use of artificial viscosity tends, however, to introduce some inaccuracy. Other workers have therefore used the FCT method with Eulerian gas dynamics. Amongst these are van den Berg (1980), with the BLAST code, and Guirao, Bach and Lee (1979) and H. Phillips (1980).

This work on numerical simulation of vapour cloud explosions has produced a number of significant results. One concerns the fraction of the heat of combustion which is converted into blast energy, or mechanical work done on the surrounding gas/air; in other words, the yield factor of the explosion. In the work of Fishburn (1976) this fraction was found to be 38%. Guiraio, Bach and Lee (1979) performed a study in which they compared a volumetric fuel–air explosion and a fuel–air detonation, and confirmed the finding of Oppenheim *et al.* (1977) that the difference in the fraction of energy converted to blast is small.

Strehlow *et al.* (1979) made an extensive numerical study of the properties of a blast wave for constant velocity flames over a wide range of flame speeds in spherical symmetry. They found that the calculated blast effects from the simulation, using as the constant flame speed the highest value observed, did not exceed the observed blast effects. This work was the basis of the Baker–Strehlow model, as already described.

The basic approach in this work has been to treat combustion as a fixed addition of energy at the particular flame speed. This does less than justice to the interaction of flow, combustion and turbulence and the associated positive feedback which occurs. The work of Hjertager (1982) advanced the art with a more fundamental treatment of transient compressible turbulent flow with reaction. It has given rise to two major CFD codes, FLACS and EXSIM.

An illustrative example of the use of the EXSIM code is given in Appendix F of the CCPS *Fire and Explosion Model Guidelines* (1994/15). The problem considered is combustion of a vapour cloud released amongst items of equipment on a plant in the open. The results include pressure versus time and flame speed versus distance profiles and contours of gas concentration, overpressure and wind velocity broadly similar to those shown in Plate 28.

Other codes include REAGAS, described by van den Berg (1989), and CLICHE, described by Catlin (1990).

17.28.28 Hydrogen explosions

Vapour clouds of hydrogen are somewhat unusual and need separate treatment. An account of hydrogen vapour cloud explosions has been given by Bulkley and Jacobs (1966).

These authors describe a number of incidents in which hydrogen–air explosions have occurred. Of particular importance is an explosion which took place during the intentional release of hydrogen from Los Alamos Scientific Laboratory at Jackass Flats, Nevada, in 1964 and which has been described by Reider, Otway and

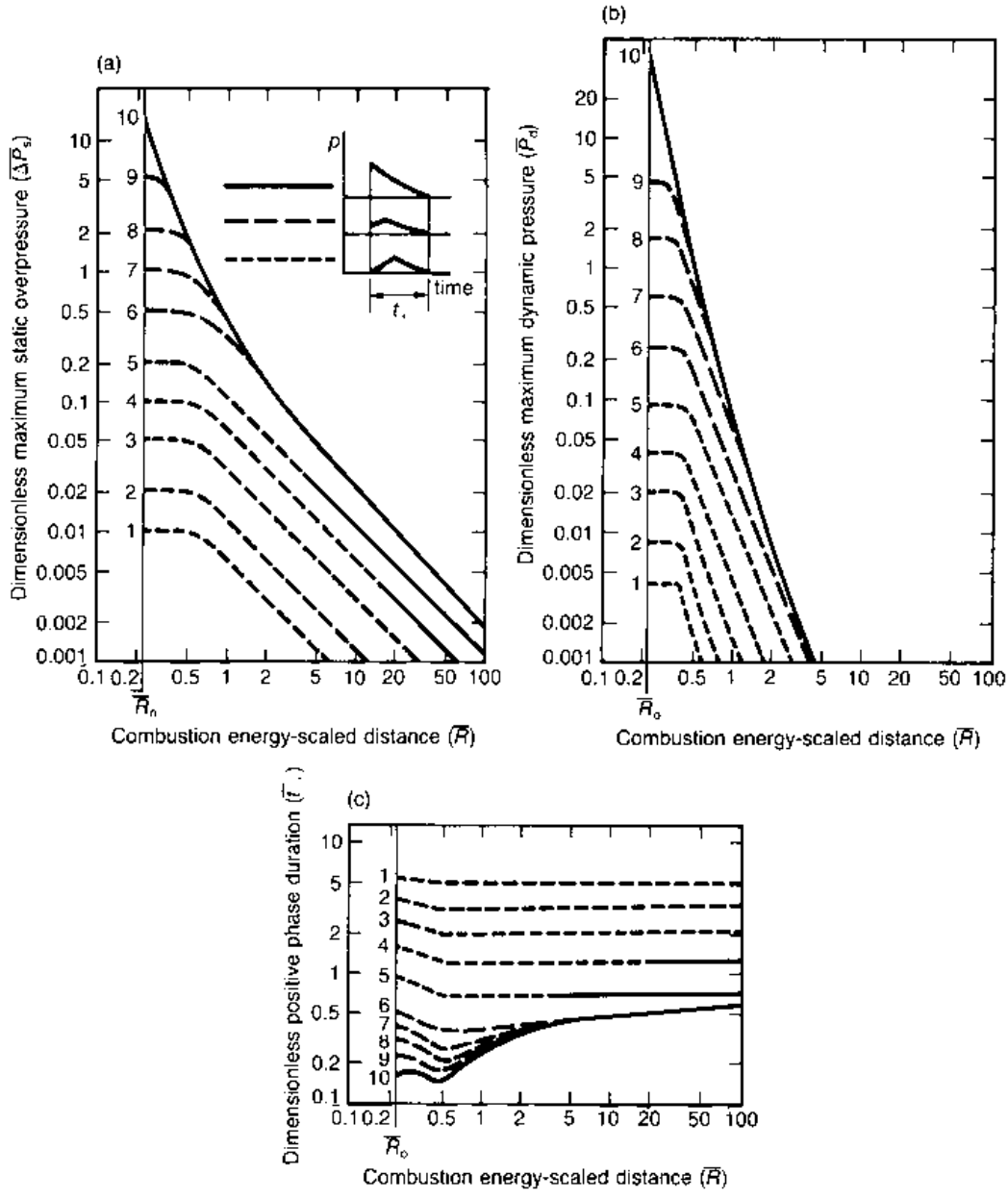


Figure 17.79 *TNO multi-energy model for vapour cloud explosions (van den Berg, 1980): (a) peak overpressure; (b) dynamic pressure; and (c) duration. c_o = ambient velocity of sound, E = combustion energy, P_d = dynamic pressure, P_o = ambient pressure; R_o = fuel–air charge radius, t_+ = duration time, $\bar{P}_d = P_d/P_o$, $\Delta\bar{P}_s = \Delta P_s/P_o$, $\bar{R} = R(P_o/E)^{\frac{1}{3}}$, $\bar{t}_+ = t_+ c_o (P_o/E)^{\frac{1}{3}}$ (Courtesy of Elsevier Science Publishers)*

Knight (1965). The incident was recorded by high speed photography. The discharge rate had been at a peak of 430 000 lb/h but had been cut back to 125 000 lb/h when spontaneous ignition occurred. The resulting explosion was estimated to have caused a pressure wave of 0.5 psi at buildings less than 200 ft way. From the photographs it was estimated that the cloud of hydrogen–air mixture which took part in the explosion was 30 ft in diameter and 150 ft high and contained 200 lb of hydrogen and that the flame speed reached 100 ft/s. The flame speed was thus considerably above the normal burning velocity but had not reached detonation velocity.

On the assumption that one-fifth of the heat released is converted to blast energy, Bulkley and Jacobs calculate that 1 lb of hydrogen can give a blast effect equivalent to 5 lb of TNT, provided detonation occurs.

They state, however, that if a detonation does not occur, then the results from the Jackass Flats incident indicate that the distances for a particular blast intensity calculated using this TNT equivalent are overestimated by a factor of about 4.

Hydrogen is frequently vented to the atmosphere. Bulkley and Jacobs present results of calculations on the flow rates which might give rise to 10 lb of hydrogen in the flammable range. They estimate that the detonation of 10 lb of hydrogen could cause severe structural damage at about 150 ft and moderate structural damage at about 300 ft. Assuming that the exit velocity is of the order of 1000 ft/s, calculations for free jets indicate that the inventory of hydrogen in the flammable range would be equivalent to 2–8 s of flow and that therefore the hydrogen flow should not exceed 4000–18 000 lb/h if excessive damage is to be avoided. The account of the Jackass Flats explosion by Reider, Otway and Knight mentions that the hydrogen is normally flared off if the release flow exceeds 3600 lb/h.

Emergency releases of hydrogen-rich streams of 50 000–150 000 lb/h are not uncommon.

Many releases are not pure hydrogen, but also contain hydrocarbons. The addition of hydrocarbons narrows the flammable range and reduces the burning velocity. It may also increase the volume of flammable mixture necessary for detonation. On the other hand, it also increases the molecular weight, which means that the jet maintains its integrity longer, so that the volume of flammable mixture is greater, and it increases the energy per unit volume. The overall result is uncertain, but Bulkley and Jacobs suggest that it is prudent to assume that a hydrogen-rich stream has the same hazard potential as one of pure hydrogen.

The authors discuss hydrogen venting, and suggest that emergency venting flows be reviewed and that if high vent flows may occur they should either be released directly to the atmosphere via multiple vents or should be flared.

Other incidents described include two disasters with hydrogen-filled dirigible airships. These are the disaster of the R-38 at Hull in 1921, in which there was an explosion, and that of the LZ-19, the *Hindenburg*, at Lakehurst, New Jersey, in 1937, in which the hydrogen burned with no overpressure. The fatalities in these two accidents were 44 and 36, respectively.

A method of estimating the peak overpressure from hydrogen explosions has been given by Hawksley (1986 LPB 68). The method is applicable to a typical, relatively small release. The two scenarios considered are a jet and a buoyant plume. The mass of fuel in the vapour cloud is determined using modifications of the equations given by J.G. Marshall (1980). The peak overpressure is then obtained from the TNT equivalent model using an explosion yield of 4%.

Hydrogen explosions are also discussed by V.C. Marshall (1987), who deals particularly with hydrogen-filled airships. He gives data showing the ultimate fate of some 129 airships. Of these, 41 (33.5%) caught fire or were set on fire by enemy action, 20 (15%) in flight and 21 (16%) in their sheds, whilst three (2.5%) exploded in flight.

17.28.29 Methane and LNG combustion

Large quantities of methane are handled as LNG, and the behaviour of methane and LNG vapour clouds is therefore of particular interest.

There is now considerable evidence that vapour clouds of methane at normal temperatures burn, but do not readily explode. Many experiments have been done in which attempts have been made to initiate explosions in methane clouds, but in which no explosion occurred.

The occurrence of vapour cloud explosions involving methane has been reviewed by V.C. Marshall (1987). He cites expert opinion to the effect that there has been no case of an unconfined vapour cloud explosion with natural gas, but also the account given by Gugan (1979) of an explosion involving methane at Raunheim, West Germany, in 1966.

It may be noted that in the First *Canvey Report* (HSE, 1978b) it was conservatively assumed that a vapour cloud of LNG might explode.

17.28.30 Explosion yield limit

As already stated, in vapour cloud explosion work the fraction of the energy of combustion which is converted to blast energy is frequently expressed as a TNT equivalent.

The generally quoted limit for this fraction is about 40%. This is the value given, for example, by the CCPS (1994/15), which also refers to numerical simulation work in which the highest fraction obtained was 38%, as described above.

In his work on vapour cloud explosions, Gugan (1979) gave equations and listed incidents for which the TNT equivalent was cited as above 50%. Ale and Bruning (1980) took issue with this on the basis that it violated the law of thermodynamics governing the conversion of energy into mechanical work. The matter was further considered by H. Phillips (1981b).

The difficulty appears to lie in the use of the TNT equivalent. In an investigation of an explosion incident the equivalent mass of TNT is obtained by examining the damage effects. It does not follow, however, that for a given level of damage the explosion energies in a TNT explosion and a vapour cloud explosion are the same. A TNT explosion involves a very high drop in overpressure in the near field and a shorter impulse. In other words, the energy released in a TNT explosion may be less effective in causing damage than that in a vapour cloud explosion.

Further, there are uncertainties in the peak overpressure for a TNT explosion and in the correlation of damage effect with peak overpressure. Phillips states that differences in blast correlations can introduce a factor of as much as an order of magnitude.

A vapour cloud explosion may therefore have an apparent TNT equivalent greater than 40% even if the actual fraction of the energy of combustion converted to blast energy does not exceed that value.

17.28.31 CCPS method

The CCPS *Fire and Explosion Guidelines* (1994/15) include a set of methods for vapour cloud explosions. Both TNT equivalent and fuel–air models are given. For

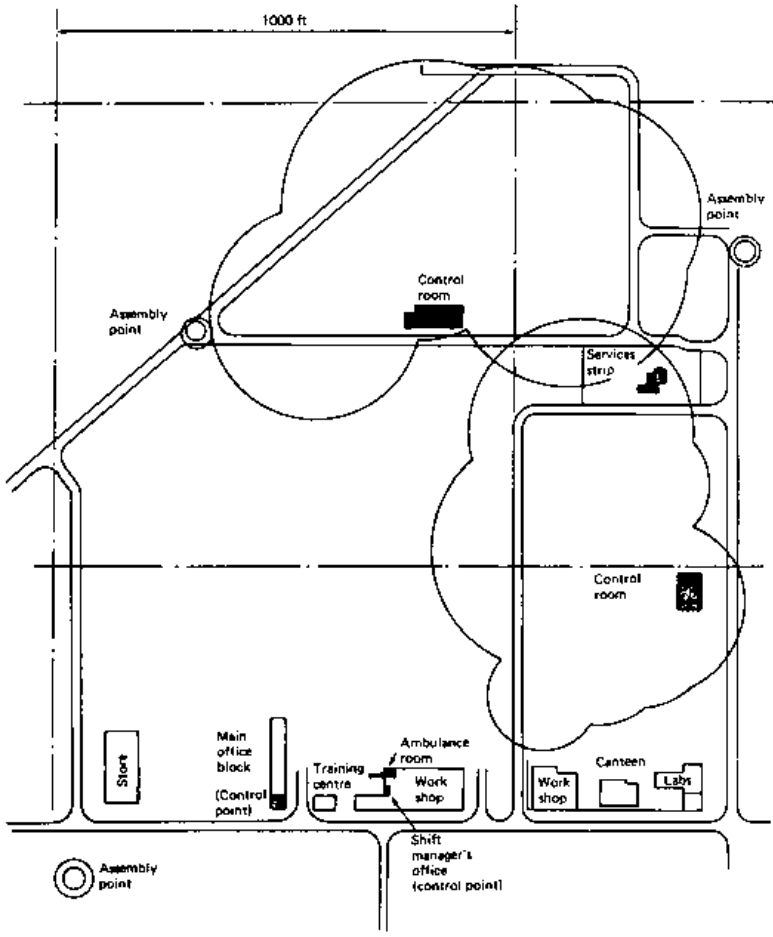


Figure 17.80 *Petal diagram showing areas affected by possible vapour cloud explosions (Kletz, 1977j) (Courtesy of the Institution of Chemical Engineers)*

the TNT equivalent method use is made of Equation 17.28.6. The sample problem utilizes an energy of explosion of TNT of 4650 kJ/kg and a yield of 0.03. The fuel–air models used are the Baker–Strehlow model, the Wiekema expanding piston model and the van den Berg ME model.

The *Guidelines* give two sample problems, one a hazard assessment of a vapour cloud explosion at a storage site and the other an assessment of the overpressure at Flixborough. To each of these they apply both the TNT equivalent model and the ME model.

17.28.32 Plant design

The vapour cloud explosion hazard may be mitigated by plant design. Two aspects which have been considered particularly are limitation of the size of potential releases and the layout of plant to deal with the effects of any explosion.

For some plants handling flammable liquids the avoidance of large-bore pipes which could, if ruptured, give a large release has been a specific design objective.

In plant layout, suitable separation distances may be used to decrease the likelihood of unacceptable damage, while buildings such as control rooms which may be affected can be suitably designed. The effect of a possible vapour cloud explosion in a works may be explored by assuming the explosion of vapour clouds of different sizes and degrees of drift and constructing diagrams showing the areas affected by blast, or 'petal diagrams'. A petal diagram given by Kletz (1977j) is shown in Figure 17.80. Guidelines on plant layout for vapour cloud explosion hazard were given in Chapter 10.

17.29 Boiling Liquid Expanding Vapour Explosions

Another of the most serious hazards in the process industries is the boiling liquid expanding vapour explosion (BLEVE). Generally, this occurs when a pressure

vessel containing a flammable liquid is exposed to fire so that the metal loses strength and ruptures.

Accounts of boiling liquid expanding vapour explosions have been given by Kletz (1977j), Reid (1979), A.F. Roberts (1981/82, 1982), Manas (1984), Pietersen (1985), Skandia International (1985), Blything and Reeves (1988 SRD R488), Selway (1988 SRD R492), D.M. Johnson and Pritchard (1991) and the CCPS (1994/15).

When a vessel containing liquid under pressure is exposed to fire, the liquid heats up and the vapour pressure rises, increasing the pressure in the vessel. When this pressure reaches the set pressure of the pressure relief valve, the valve operates. The liquid level in the vessel falls as the vapour is released to the atmosphere. The liquid is effective in cooling that part of the vessel wall which is in contact with it, but the vapour is not. The proportion of the vessel wall which has the benefit of liquid cooling falls as the liquid vaporizes. After a time, metal which is not cooled by liquid becomes exposed to the fire; the metal becomes hot and weakens and may then rupture. This can occur even though the pressure relief valve is operating correctly. A pressure vessel is designed to withstand the relief valve set pressure, but only at the design temperature conditions. If the metal has its temperature raised, it may lose strength sufficiently to rupture.

Most BLEVEs involve a pressure storage vessel, rail tank car or road tanker containing a flammable liquid, typically a liquefied flammable gas, which becomes exposed to a fire or flame, and in due course ruptures, often giving a fireball. Another common situation which gives rise to a BLEVE is a derailment. The development of the BLEVE is illustrated in Figure 17.81. A pressure relief valve on one tank car operates, the release ignites and the flame plays on another tank car. The liquid in this vessel heats up, the pressure rises and the relief valve operates, the release being ignited by the flame playing on the vessel. For a time the metal of this vessel is kept cool by liquid in contact with it, but the level falls as the liquid is vaporized, metal cooled only by vapour is exposed, becomes hot, weakens and ruptures. A large fraction of the flammable liquefied gas released, vaporizes and forms a burning vapour cloud, often a fireball.

A BLEVE of a vessel containing a flammable liquid gives rise to the following effects: (1) blast wave, (2) fragments and (3) fireball.

Following Flixborough much attention was focused on VCEs. It was pointed out by Kletz (1977j) that BLEVEs can cause as many casualties as VCEs and that by comparison they were being relatively neglected. This view has been amply justified by the subsequent record.

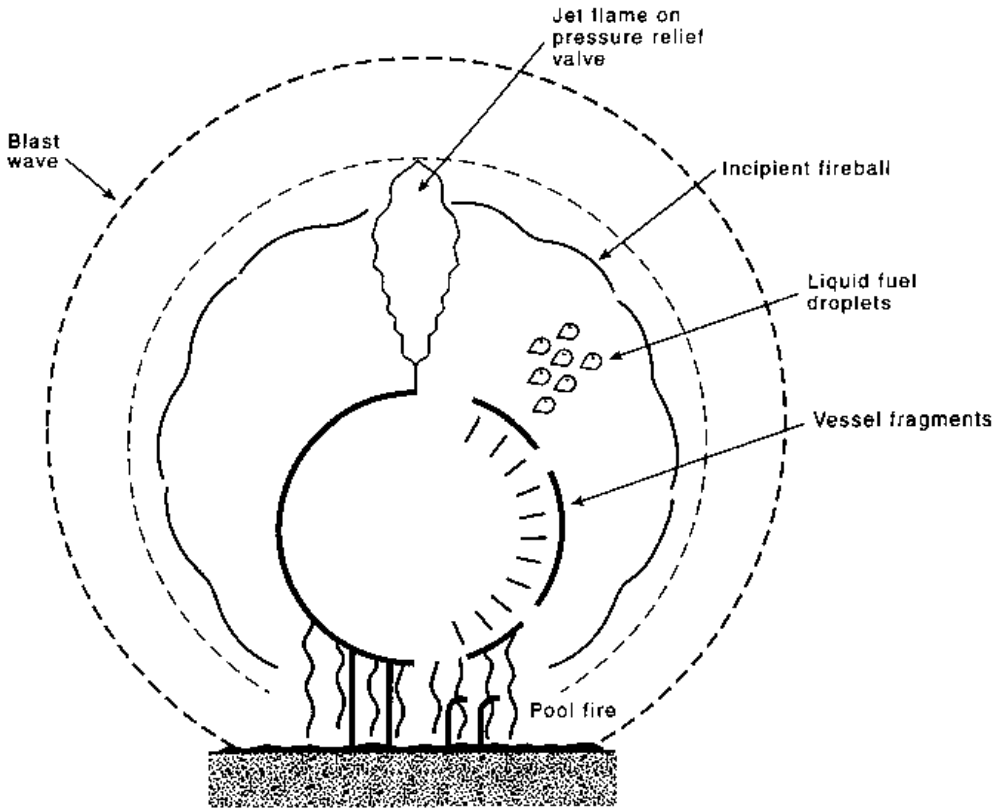


Figure 17.81 *A BLEVE event*

Selected references on BLEVEs are given in Table 17.36.

Table 17.36 *Selected references on boiling liquid expanding vapour explosions (BLEVEs)*

CEC (n.d./1); Exxon (n.d.); C. Andersen and Norris (1974); Hess, Hoffman and Stoeckel (1974); M.R. Johnson *et al.* (1974); Kletz (1977d, 1981n); Maurer *et al.* (1977); Buivid and Sussman (1978); Walls (1978, 1979); R.C. Reid (1979, 1980); A.F. Roberts (1981/82, 1982); Considine, Grint and Holden (1982); Crawley (1982); Pantony and Smith (1982); Blything (1983 SRD R263, 1986); A.F. Roberts, Cutler and Billinge (1983); Solberg and Borgnes (1983); Manas (1984); Martinsen (1984); Tunc and Venart (1984/85a,b); D.L.M. Hunt and Ramskill (1985); D.J. Lewis (1985); Pietersen (1985, 1986a,b); Skandia (1985); Johannson (1986); Martinsen *et al.* (1986); Pitblado (1986a); McDevitt, Steward and Venart (1987); Skarka (1987); Blything and Reeves (1988 SRD R488); Holden (1988 SRD R477); Nazario (1988); Selway (1988 SRD R492); J.B. Moss (1989); Lemoff (1989); McDevitt *et al.* (1990); Venart (1990a); D.M. Johnson and Pritchard (1991); Pineau *et al.* (1991); Prugh (1991); Scilly and Crowther (1992); Melham, Croce and Abraham (1993); Venart *et al.* (1993); Birk and Cunningham (1994)

17.29.1 BLEVE incidents

Compilations of BLEVE incidents are less numerous and comprehensive than those for VCEs. The principal lists are those of Pietersen (1985), Skandia International (1985) and Selway (1988 SRD R492). Incident data are also available from the MHIDAS databank of the SRD.

Some principal BLEVE incidents are given in Table 17.37. Other incidents are listed in Table A1.2.

The BLEVE at Feyzin on 1966 has received particular attention (Case History A38). In this incident an operator draining water from the bottom of a propane sphere lost control. A vapour cloud formed, ignited and flashed back to the vessel. The pressure in the vessel rose and the relief valve lifted, but the metal of the vessel lost strength and some 90 min after ignition the vessel burst. The death toll was 18. Plate 32 shows one of the fire engulfed spheres.

A remarkably similar event took place at the Duque de Caxais refinery at Rio de Janeiro in 1972 (Case History A61). Again an operator lost control of a draining operation on an LPG sphere, a vapour cloud formed, ignited and flashed back to the sphere, engulfing it in fire, so that after about 15–20 min it suffered a BLEVE.

In these incidents the release at, and BLEVE of, the vessel was the initial event. There have also been instances where a release from one storage vessel has led to a fire which has caused BLEVE of an adjacent one. Such was the case at Montreal, Quebec, in 1957, when overfilling of a butane sphere caused a release which led to a pool fire (Case History A25).

In 1978 at Texas City, Texas, overfilling of an LPG sphere led to a fire which caused the BLEVE of an adjacent sphere.

In other cases BLEVEs have occurred due to engulfment in a vapour cloud fire. Such a fire occurred at Port Newark, New Jersey, in 1951 and led to the destruction of over 70 bullet tanks, many by BLEVE (Case History A19).

Engulfment in a vapour cloud fire was also the cause of destruction, largely by BLEVE, of four storage spheres and 48 cylindrical vessels holding LPG at Mexico City, Mexico, in 1984. Some 500 people were killed. This incident, shown in Plate 35, is described in Appendix 4.

BLEVEs also happen in transport, typically when flammable material is released and ignited following an accident, so that a transport tank becomes engulfed in fire. They have occurred particularly on rail tank cars, often when a jet flame from the relief valve on one tank has played on another.

A derailment of nine rail tank cars at Crescent City, Illinois, in 1970 caused a release of propane which led to a fire and caused a succession of tank car BLEVEs (Case History A50). The BLEVEs were accompanied by large fireballs and missiles, including rocketing tanks. One of the fireballs is shown in Plate 33.

Other rail tank car BLEVEs include those at Laurel, Mississippi, in 1969 (Case History A44), Houston, Texas, in 1971 (Case History A53), Kingman, Arizona, in 1973 (Case History A63), Oneonta, New York, and West St Paul, Minnesota, in 1974, Des Moines, Iowa, in 1975, Belt, Montana in 1976 and Livingston, Louisiana, in 1982 (Case History A103). Road tank car BLEVEs include those at Lynchburg, Virginia, in 1972 (Case History A59) and Los Angeles, California, in 1979.

17.29.2 The BLEVE event

The essential features of a BLEVE are that (1) the vessel fails, (2) the failure results in flash-off of vapour from the superheated liquid and, if the liquid is flammable, (3) the vapour ignites and forms a fireball.

The accompanying effects are (1) blast, (2) fragments and, for flammable liquids, (3) a fireball.

The BLEVE creates an overpressure. This phenomena associated with this are (1) the expansion of the vapour, (2) the flash vaporization of the liquid and, for flammable liquids, (3) the combustion of the vapour. These events are not completely simultaneous, but have been measured as separate effects.

A BLEVE usually generates missiles. These may be fragments created by the rupture event and also the body of the vessel itself. The pressure at the instant of burst is high and the reaction force is often large enough to cause the main part of the vessel to rocket.

A BLEVE resulting from the fire engulfment of a vessel containing a flammable liquid also gives rise to a fireball.

An account of the origin of the term 'BLEVE' is given by the CCPS (1994/15), which states that the term was introduced by workers at the FMRC. An early account of the phenomenon was that of Walls (1979) at the National Fire Protection Agency (NFPA).

Although most BLEVEs of interest here involve a liquid which is flammable, this is not a necessary feature of a BLEVE. The rupture of a vessel containing superheated water can constitute a BLEVE. Likewise, although engulfment in fire is the common cause of BLEVE, it too is not a necessary feature. Any rupture of a vessel containing a superheated liquid may be termed a BLEVE.

It is possible, therefore, though not common, for a BLEVE event not caused by an engulfing fire to provide

Table 17.37 *Some BLEVE incidents*

A BLEVE incidents

Date	*Location*	*Material*	*Plant/transport involved*	*Deaths/ injuries*	*Fireball*	
					Quantity released (te)	*Radius* (m)
1951	Port Newark, NJ	LPG	Storage cylinder (70 on site)	14i		
1955	Ludwigshafen, FRG		Rail tank car	2i		
	Cottage Grove, OR	LPG	Storage vessel	12d, 12i		
1958	Celle, FRG		Rail tank car			
1957	Montreal, Quebec	Butane	Storage sphere	1d		
1959	McKittrick, CA	LPG	Storage cylinder (6 on site)	2i		
1966	Feyzin, France	LPG	Storage sphere (8 on site)	18d, 81i		
1968	Dunreith, IN	Ethylene oxide	Rail tank car	5i		
1969	Laurel, MS	LPG	Rail tank car (derailment, 15 cars)	2d, 976i(?)		
1970	Crescent City, IL	Propane	Rail tank car (derailment, 9 cars)	66i	75	75–100
1971	Houston, TX	VCM	Rail tank car (derailment, 18 cars)	1d, 50i	165	150
1972	Lynchburg, VA	Propane	Road tanker	2d, 5i	9	60
	Rio de Janeiro, Brazil	LPG	Storage spheres (5 on site) and cylinders	37d, 53i		
1973	Kingman, AZ	Propane	Rail tank car	13d, 95i	45	150
1974	Bielefeld, FRG		Rail tank car (derailment, 36 cars)			
	Oneonta, NY	LPG	Rail tank car	25i		
	West St Paul, MN	LPG	Storage vessel	4d	10	50
1975	Des Moines, IA	LPG	Rail tank car	3i		
1976	Belt, MN	LPG	Rail tank car	22i	80	150
1977	Dallas, TX	Isobutane	Rail tank car	1i		
1978	Texas City, TX	LPG(?)	Storage vessel	7d, 10i		
	Waverly, TN	Propane	Rail tank car	16d, 43i		
1979	Paxton, TX	Chemicals	Rail tank car	8i		
	Los Angeles, CA	Gasoline	Road tanker	2d, 2i		
1982	Livingston, LA	Flammables	Rail tank car	0d, 0i		
1984	Romeoville, IL	Propane	Process vessel	15d, 22i		
1985	Mexico City, Mexico	LPG	Storage spheres and cylinders	≈650d, ≈6400i		

B Fireball incidents

Date	*Location*	*Material*	*Plant/transport involved*	*Deaths/ injuries*	*Fireball*	
					Quantity (te)	*Radius* (m)
1956	Amarillo, TX	Oil	Storage tank	20d, 32i		
1974	Aberdeen, UK	Butane	Road tanker		2	35
1975	Eagle Pass, TX	LPG	Road tanker	17d, 34i		
1976	Gadsden, AL	Petrol	Tank farm	4d, 28i		
1977	Goldona, VA	LPG	Rail tank car	2d, 9i	70	160
1978	Donnellson, IA	LPG	Pipeline	2d, 2i (?)	435	305
	Lewisville, AR	VCM	Rail tank car	2i	110	155

the source for a large vapour release, leading to a flash fire or VCE.

A review of events which can lead to a BLEVE has been given by Prugh (1991), who gives the term a fairly wide interpretation and lists the following: (1) fire exposure, (2) mechanical damage, (3) overfilling, (4) runaway reaction, (5) overheating, (6) vapour space explosion and (8) mechanical failure.

17.29.3 Experimental studies

As described in Chapter 16, there have been a number of experimental studies of fireballs. The BLEVE event as a whole has not been so well served.

C. Anderson *et al.* (1975) describe work at the Association of American Railroads (AAR) on fire engulfment of a 125 m^3 rail tank car which suffered a BLEVE.

Experimental work on BLEVEs has been described by Hardee and Lee (1975), who did tests involving 420 kg of propane and modelled the processes of bursting and mixing with air.

Tests on vessel bursts directed to the same end are given by Maurer *et al.* (1977), but these authors also report measurements of the overpressure associated with the burst, as described in Chapter 15.

Work in the same series is that described by Giesbrecht *et al.* (1980), who used 450 kg of propylene and modelled the bursting, mixing and combustion processes.

Work at the Bundesansalt für Materialprüfung (BAM) on fire engulfed vessels containing liquid propane, described by Schulz-Forberg (1984), Droste and Schoen (1988) and Schoen, Probst and Droste (1989), involved tests on 4.84 m^3 tanks with generation of fireball and fragments.

Further larger scale experiments have been performed at British Gas by D.M. Johnson and Pritchard (1991). Their base case was a 5.66 m^3 vessel containing 2 te of butane at a pressure of 15 barg. They performed five tests, with the base case and with the following four variations: (1) lower mass, (2) lower pressure, (3) different vapour/liquid ratio and (4) using propane. Vessel failure was effected by explosive charges and ignition was by propane lances.

The purpose of this BG work was to investigate the overpressure and thermal radiation. With regard to overpressure, the authors state that the vapour expansion and flash vaporization tended to merge. The overpressure from vapour expansion agreed well with predictions for overpressure from a bursting vessel. The overpressure from flash vaporization was substantially less than that predicted, apparently because the liquid temperature was below that required to give homogeneous nucleation, or superheat limit.

The overpressure from the combustion came somewhat later and had a much longer duration, of the order of 100–300 ms. The overpressure trace which the authors give shows the maxima of the two overpressure pulses to be comparable. These traces show the overpressures measured at 150 m from the vessels to have been of the order of 4 mbar. The authors state, however, that the combustion overpressure was often greater.

With regard to the fireball, this showed in some tests an appreciable degree of asymmetry. For the mass of fuel in the fireball, the authors quote the limit of 35% theoretical flash vaporization above which flash-off of the whole contents is often assumed. The theoretical flash in their work was over 45% and complete flash-off was assumed. This was supported by the visual records, which showed only small amounts of liquid fuel burning on the ground.

The fireball diameter and duration were broadly as predicted by models such as that of A.F. Roberts (1981/82). Except in one test the height of the centre of the fireball was between 0.8 and 1.35 times the equivalent maximum diameter, which compares with the suggestion by Moorhouse and Pritchard (1982) that it be taken as the maximum diameter.

For the thermal radiation from the fireball, the surface emissive power was somewhat higher than values commonly quoted, with peak values up to 500 kW/m^2 and the remainder in the range 250–350 kW/m^2.

The CCPS (1994/15) describes one of the BAM and one of the British Gas tests and states that the liquid temperature exceeded the superheat limit in the former but not in the latter.

Melham, Croce and Abraham (1993) describe a series of BLEVE tests carried out by the NFPA in conjunction with the production of a successor to its earlier film 'BLEVE', entitled 'Bleve Update'. The purpose of the tests was to establish a database of experiments and to obtain film of BLEVE events. There were six tests, two each with a simulated pool fire, an impinging gas jet flame and an impinging liquid jet flame. The vessels tested were 1.89 m^3 propane tanks. In these tests peak overpressures up to 37 kPa were measured at a distance of 15 m from the tanks.

17.29.4 Empirical features

It is also helpful to consider some features of BLEVEs from an empirical viewpoint. Those discussed here are (1) the time to BLEVE, (2) the mode of rupture, (3) the blast effects, (4) the fireball, (5) the missiles and (6) the release of flammable fluids. Time to BLEVE is treated in the following subsection and the other items here.

With regard to the mode of rupture, cylindrical tanks usually rupture longitudinally, though some rupture circumferentially. The latter particularly tend to take off like rockets and may travel long distances. This was true of some of the cylindrical tanks at Mexico City. Spheres often explode, but in some cases may simply split at the top as occurred both at Feyzin and Mexico City.

The pressure at the instant of rupture must approximate to that in the vessel. Generally, therefore, it will be appreciably greater than that at the centre of a VCE, which is commonly estimated to have a maximum overpressure of about 1 bar. Thus in a BLEVE the overpressure at the vessel at the instant of rupture may be an order of magnitude higher than that at the centre of a VCE. The blast wave from a BLEVE can cause damage. At Feyzin the blast wave caused extensive though minor damage in a village 500 m away and broke some windows at a distance of 3 km.

The flammable vapour released forms a fireball. The fireball can be large and it can rise to an appreciable height. Fireball diameters at Mexico City are estimated from film records to have been of the order of 200 or 300 m with a duration time of some 20 s. The fireball at Crescent City rose to a considerable height, as shown in Figure A1.4 (see Appendix 1).

At Mexico City there was also a fire column which resembled a huge flare rather than a fireball and which film records show to have lasted 90 s.

The maximum distances at which injury due to heat radiation has been reported are 300 m at Feyzin and 400 m at Mexico City, while the maximum distance at which death has been reported is 300 m at Kingman.

Survivals have been reported at distances comparable with the estimated radius of the fireball. At Belt the reported fireball diameter was 1000 ft. The calculated diameter is 540 ft, based on the 80 te of flammable material believed to have been involved, though there is some doubt on this quantity. Firemen within 200 ft survived (Kletz 1981n). Further details of survival at this and ofireballs are given by Crawley (1982).

BLEVEs tend to generate massive missiles, including the main part of the vessel. Missiles from BLEVEs are considered in more detail in Section 17.34, but brief mention is made here. At Feyzin the sphere BLEVE generated five large fragments, of which three each had a mass of over 100 te and were thrown distances of 150–350 m. One piece knocked over another sphere which itself in due course underwent a BLEVE.

The BLEVEs which occurred in the vapour cloud fires at Port Newark in 1951, Texas City in 1978 and Mexico City in 1984 all generated large missiles. At Port Newark one large tank section about 17 m long was hurled over half a mile and demolished a petrol filling station. At Mexico City the spheres generated 25 major fragments which travelled 100–590 m, whilst one bullet tank was propelled 1200 m. This latter appears to be the maximum distance travelled by a BLEVE missile.

The liquid in the vessel does not necessarily vaporize completely. At Tewkesbury, Massachusetts, in 1972 some 35% of the propane flashed off, the remaining liquid being scattered in all directions.

BLEVEs do not generally to give rise to VCEs. But they may scatter flammable liquid spray which gives a spray fire and/or falls on people and property, rendering them more flammable and liable to ignition. Hot missiles may also cause fires.

17.29.5 Time to BLEVE

The time between the occurrence of an engulfing or torch fire and BLEVE is of significance not just for the general characterization of BLEVEs but for the design of fire systems to protect against them and for fire fighting.

For the sphere at Feyzin in 1966 the time between ignition of the leak and vessel rupture was about an hour and a half. This time to BLEVE is much longer than in most other incidents.

More commonly, for storage vessels the time to BLEVE has been of the order of 5–30 min. A period of 3–10 min was observed for some vessels at Montreal, McKittrick and Mexico City. A time of some 30 min was observed for other vessels at these three incidents.

Hazard assessments of storage vessels in respect of BLEVE have been made by Blything and Reeves (1988 SRD R488) and Selway (1988 SRD R492). Blything and Reeves studied a horizontal cylindrical storage vessel holding butane, with a nominal capacity of 100 te and actually holding 85 te, being thus 75% full. They considered scenarios involving (1) partial fire engulfment and (2) jet flame impingement, and obtained for time to BLEVE estimates of between 4 and 48 min.

Selway describes an equivalent study for a 2000 m^3 storage sphere containing some 1000 te of LPG when full. For scenarios of total fire engulfment, partial fire engulfment and jet flame impingement he obtained times to BLEVE of 7–11, 25–38 and 5.5–7 min, respectively. These times are a function of the degree of fill. A vessel which is empty has a much shorter time, whereas the difference in times between a vessel which is half full and one which is full is small. Thus, for example, for the partial engulfment case, the times to BLEVE given for the states virtually empty, half full and full are 25, 36 and 38 min, respectively.

Times to BLEVE for tanks in transport accidents, particularly rail tank cars, have also been mainly in the range 5–30 min.

17.29.6 Vessel burst pressure

The explosion energy released in BLEVE is a function of the initial pressure.

The various different scenarios for vessel burst pressure have been discussed in Section 17.27, where a distinction was made between the following causes: (1) operating overpressure, (2) mechanical failure and (3) fire engulfment.

17.29.7 Liquid superheat limit

The energy of the explosion which is part of the BLEVE event depends on the conditions in the vessel. In particular, under certain conditions, explosive flashing of the superheated liquid can occur, giving a large release of energy.

The explanation of what happens which has received most acceptance is the liquid superheat limit theory of Reid (1976, 1979, 1980). If a liquid has a sufficient degree of superheat and the pressure on it is suddenly removed, microscopic vapour bubbles form and a large fraction flashes off within milliseconds.

The degree of superheat necessary for this effect to occur is determined by the homogeneous nucleation temperature, or superheat limit temperature. There are a number of correlations for this, which differ according to the equation of state used. Using van der Waals's equation of state, Opshoor (1974) obtained

$$T_{sl} = 0.84T_c \qquad [17.29.1]$$

whilst using the Redlich–Kwong equation of state Reid (1976) obtained

$$T_{sl} = 0.895T_c \qquad [17.29.2]$$

where T_c is the critical temperature (K) and T_{sl} the superheat limit temperature (K).

Reid also confirmed that for a wide range of industrial substances the coefficient in Equation 17.29.2 lies within the range 0.89–0.90.

Reid studied particularly the superheat limit temperature of propane, for which the value generally quoted is 53°C. The values given by Equations 17.29.1 and 17.29.2 38°C and 58°C, respectively.

Data on the liquid superheat limit temperature are given by Lide (1994). Where it is necessary to predict it, use is generally made of Equation 17.29.2.

Other mechanisms to explain explosive flashing have been suggested. Board *et al.* (1975) apply the superheat limit concept in conjunction with that of atomization of the liquid by shock waves at the vapour-liquid interface,

whilst Venart (1990a) combines the concept with the effect of the depressurization–repressurization cycles associated with the operation of a pressure relief valve.

If the degree of superheat is not sufficient to promote explosive flashing, the energy release in a BLEVE is that due to the pressure energy in the vapour space, which is generally an order of magnitude less.

The superheat limit model of a BLEVE is discussed further in Section 17.29.9.

17.29.8 Modelling of BLEVEs

There are several different approaches to the modelling of BLEVEs. They include (1) the superheated liquid explosion model, (2) the the cloud formation model and (3) bursting vessel model.

The modelling of a BLEVE is closely related to the modelling of a fireball, as described in Chapter 16.

17.29.9 Superheated liquid explosion model

The superheated liquid explosion model is that of Reid, which has been outlined in Section 17.29.7. Reid suggests that this theory may explain the behaviour of the liquid at the moment of BLEVE.

The application of the theory to a BLEVE may be explained by considering the specific case of the depressurization of a vessel containing propane. The vapour pressure and superheat limit lines for propane are given in Figure 17.82. The superheat limit is the limit to which propane may be heated before spontaneous nucleation occurs, giving a vapour explosion. Prior to the accident the propane is at an absolute pressure of 8–9 atm and ambient temperature at point A on the graph. In the accident conditions the liquid is heated up by the fire on the vessel. The behaviour of the liquid then depends on the temperature which it has reached when rupture and sudden depressurization occur. If depressurization occurs when the temperature is that corresponding to point B, the pressure will fall to atmospheric pressure at E. There will be violent boiling but no vapour explosion, since the superheat limit line has not been reached. If depressurization occurs at point C with fall in pressure to point D, the superheat limit line is reached at about 3.3 atm, and a vapour explosion could occur. The superheat limit temperature at atmospheric pressure is thus a limit below which a superheated liquid explosion will not occur. For propane this is 53°C.

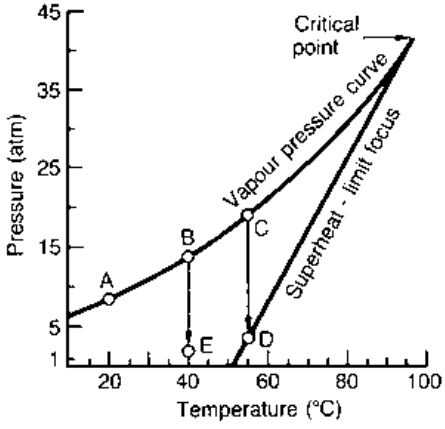


Figure 17.82 *Vapour pressure and superheat curves for propane (R.C. Reid, 1979) (Courtesy of Science)*

In support of this hypothesis Reid quotes experiments by C. Anderson *et al.* (1974) and by Hess, Hoffman and Stoeckel (1974) and a number of industrial accidents as being consistent with the hypothesis.

The theory has implications for prevention of superheated liquid explosions under these conditions. Such an explosion will not occur if depressurization occurs at a pressure corresponding to a temperature below the superheat limit temperature. The pressure relief valve may be set to operate below this pressure and thus to protect against the explosion. Another possible measure is to seed the liquid with solid particles to assist nucleation, but experimental work on these lines has not been encouraging. The measures described are addressed specifically to the mitigation of the problem of superheated liquid explosions and will not prevent explosion from other causes such as the pressure of the vapour in the vessel.

17.29.10 Cloud formation models

Models for vapour cloud formation following depressurization have been given by Hardee and Lee (1975), Maurer *et al.* (1977) and Giesbrecht *et al.* (1980) and have been compared by A.F. Roberts (1982). The first model is based on conservation of momentum with the momentum created by the liquid release appearing explicitly as a function of the initial conditions, the second model is based on turbulent diffusion and the initial conditions do not appear explicitly. Both models give similar predictions of cloud growth for releases of the order of 100 kg and have been verified experimentally at this level, but diverge for larger releases. Roberts bases his treatment on the model of Hardee and Lee.

17.29.11 Bursting vessel model

The overpressure created by a BLEVE is complex, since, as discussed above, it is in principle caused by three distinct phenomena.

The aspect where the most progress appears to have been made is in estimating the overpressure associated with the expansion of the vapour. It is suggested by W.E. Baker *et al.* (1983) that as a first approximation the blast wave from a vessel which undergoes BLEVE may be estimated by applying to the vapour space in the vessel the method, described in Section 17.27, for the bursting of a vessel filled with gas.

This approach appears to give reasonable predictions, as now described.

In order to apply this latter method it is necessary first to determine the pressure at which the vessel will burst. The following formula is quoted by Selway (1988 SRD R492) as that used in the ENGULF code for the burst pressure of a sphere:

$$P_b = 2\sigma_y \ln R\left(1 - \frac{\sigma_y}{\sigma_u}\right) \qquad [17.29.3]$$

with

$$R = r_o/r_i \qquad [17.29.4]$$

where P_b is the burst pressure, r is the vessel radius, R is the radius ratio, σ_u is the ultimate tensile strength, σ_y is the yield strength and the subscripts i and o denote inner and outer, respectively.

Pietersen (1985) has applied the method of W.E. Baker *et al.* (1983, p. 149), based on the Brode equation, for the energy in, and overpressure generated by the bursting of, a gas filled vessel to obtain the overpressure caused by the vapour expansion phase of a BLEVE, utilizing the volume of the vapour space and taking as 40% the fraction of the pressure energy which enters the blast wave. He obtains the following peak overpressures (bar) for vessels with a bursting pressure of 13.4 bar and different vapour space volumes:

Distance (m)	*Vapour space volume* (m^3)			
	20	100	800	1200
10	0.44	1.0	2.3	2.6
50	0.04	0.08	0.23	0.29
100	0.018	0.033	0.09	0.10
200	0.0075	0.012	0.033	0.04

Some experimental confirmation is provided by the finding of D.M. Johnson and Pritchard (1991) that the overpressures predicted using a model based on that for the bursting of a gas filled vessel were in reasonable agreement with those measured in their tests for the vapour expansion phase.

17.29.12 BLEVE method

An integrated BLEVE model should comprise models for the main effects of (1) blast, (2) fragments and (3) fireball. Treatments covering these aspects are given in Sections 17.27 and 17.34 and Chapter 16, respectively. The model may also include a model for fire engulfment, which is treated in Chapter 16.

17.29.13 CCPS method

The CCPS *Fire and Explosion Model Guidelines* (1994/15) give a method for the treatment of the various effects of a BLEVE. The treatment covers (1) blast, (2) fragments and (3) fireball.

For the blast the *Guidelines* method utilizes the CCPS vessel burst model, essentially that of W.E. Baker *et al.* (1975), given in Section 17.27.

The energy of explosion for use in this model is obtained by first determining whether the liquid temperature is greater than the superheat limit. Then if the superheat limit temperature is not exceeded, use is made of the Brode equation, whilst if it is, use is made of the method for flashing liquid given in Section 17.4.6. The fraction flashing off is taken as the equilibrium value yielded by the isentropic expansion.

For the fragments the *Guidelines* use the CCPS fragments model given in Section 17.33.

For the fireball the *Guidelines* use the CCPS fireball model given in Chapter 16.

The *Guidelines* devote a chapter to worked examples of BLEVE calculations. These include a problem on a fireball from a propane tank truck; problems on blast from a propane storage vessel, from a propane tank truck and at Mexico City; and problems on fragments from overpressure of a gas filled pressure vessel and from fire engulfment of a propane storage vessel.

17.29.14 Energy release and overpressure

The foregoing models provide the background for the estimation of the energy release and blast overpressure in a BLEVE. The two principal sources of energy are the compressed vapour in the vapour space and the superheated liquid as it undergoes flashing. The estimation of the energy release from these two sources has been discussed in Section 17.4. The superheat limit temperature model provides guidance on the extent to which liquid flashing is a significant contributor. A further discussion of the energy release in a BLEVE is given by Prugh (1991).

Given an estimate of the energy release, the overpressure from a BLEVE may be estimated using the methods outlined in Section 17.27.

It has been suggested by Venart *et al.* (1993) that in certain circumstances there may occur an event in which the energy release and explosion overpressure are much higher than in a regular BLEVE. This is discussed in Section 17.29.15.

17.29.15 Boiling liquid collapsing bubble explosions

The interaction between homogeneous nucleation and the vessel itself has been further investigated by Venart and coworkers (Venart, 1990a; Venart *et al.*, 1993), who have developed the concept of the boiling liquid collapsing bubble explosion (BLCBE).

The BLCBE has three aspects, involving the behaviour of (1) the liquid, (2) a crack in the vessel wall and (3) the liquid–vessel system. If the vessel wall in the vapour space is subject to heating by a flame, a crack may develop. The behaviour of this crack then depends on the degree of fill. If the fill is high, the crack may be arrested, still in the vapour space section of the wall, by plastic blunting. If the fill is lower, there may be sufficient energy in the vapour to cause the crack to propagate plastically to the cold metal, where it can then propagate elastically without restraint and with only minimal energy requirement.

This second case, with the lower fill, corresponds to the regular BLEVE. The first case has the potential for a much greater release of physical energy associated with homogeneous nucleation. If the fill is high, one of two effects may occur: (1) a massive two-phase jet or (2) a violent vessel failure with total loss of containment caused by a homogeneously nucleated liquid.

It is this second type of event in a vessel with high fill which constitutes a BLCBE. It occurs with a liquid homogeneous in temperature and depressurizing. The sequence of events is envisaged to be typically as follows. The liquid is depressurized, say by operation of the pressure relief valve, and due to this becomes nucleated. When the crack occurs, there is an almost instantaneous swell of low-void liquid which chokes in the crack. There is a rapid repressurization of the vessel contents. The resultant liquid shock pressures are very high (1–3 kbar). The crack propagates elastically through the now-cooled wall of the vapour space and on to the wall of the liquid space. The vessel fails and the highly compressed two-phase contents are again depressurized. Expansion of the high pressure vapour bubbles shatters

the liquid and results in ejection of the whole of the superheated liquid as a fine aerosol. If flammable, this aerosol may then be ignited.

Venart *et al.* (1993) describe tests in which prenucleated R112 and R123 were used and events of the type just described were observed, with destruction of the vessel in times as short as about 200 μs. They give details of the pressure effects in the vessel, including measurement of the rapid pressure transient below the liquid in excess of the static pressure in the vessel and an estimate of the instantaneous overpressure at the crack. The vessel static pressure was some 790 kPa (100 psig), the average excess pressure 490 kPa (70 psi) and the estimated overpressure at the crack itself some 62 bar (900 psig). These authors also give estimates of the diameter of the bubbles (1–3 mm), the diameter of the resultant aerosol droplets (100 μm) and the evaporation time of the droplets (40 ms). They state that there were significant blast overpressures.

These effects were obtained with a liquid temperature more than 50°C below the superheat limit temperature.

Venart *et al.* suggest that all three types of event described (regular BLEVE, two-phase jet and BLCBE) occurred at Mexico City.

They draw attention to the fact that a BLCBE may be caused by a leak, and discuss the implications of this for the leak-before-break philosophy.

17.30 Explosions in Process Plant

Some of the principal types of explosion which occur on process plant have already been described. These are explosions in chemical reactors, (2) explosions of high pressure gases inside plant, (3) explosions of flammable gas–air mixtures inside plant and in buildings, (4) vapour cloud explosions, and (5) BLEVEs.

In addition, there are certain types of explosion which may occur in particular processes, operations or equipment. Some of these have already been mentioned, such as explosions in driers, centrifuges and vaporizers, and in oxygen and chlorine plants.

Other explosion hazards include (1) aerosol explosions, (2) crankcase explosions, (3) superheated liquid explosions, (4) air system explosions and (5) molten metal–water explosions. These various types of explosion are now discussed.

17.30.1 Explosions of aerosols

Under the conditions of an accident, a cloud of finely divided drops of flammable liquid in air, in the form of a mist or spray, may be produced which has many of the characteristics of a flammable gas–air mixture and which can burn or explode.

The combustion of such aerosols has been discussed in Chapter 16, which includes treatment of flame propagation, minimum ignition energy and burning velocity. Here, consideration is given to the extent to which combustion of such clouds has the propensity to generate overpressure, and, more specifically, to undergo detonation.

As described in Chapter 16, if the droplet size of the cloud is sufficiently small, the lower flammability limit, minimum ignition energy and the burning velocity are essentially the same as those of a vapour–air mixture of the same concentration, measured in mass per unit volume.

The problem of crankcase explosions, described below, indicates that confined hydrocarbon mists can undergo explosions.

The detonation of aerosols has been discussed by Nettleton (1977b, 1987). The information available is rather limited. It has been shown that some aerosols of hydrocarbons are detonable under confined conditions. The work has been done using hydrocarbon–oxygen mixtures and there is little on mixtures with air. Information is also lacking on detonability limits, as distinct from the flammability limits, which are treated in Chapter 16.

When detonation occurs in an aerosol the detonation waves cause disintegration of the droplets. It is known that it is not necessary for the fuel to be present in extremely finely divided form for detonation to occur.

It is known also that with an aerosol the reaction zone is wider than in a homogenous mixture with consequent effects on peak pressure and duration time.

A particular type of aerosol explosion is the 'smoke explosion'. An account is given by Croft (1980/81). In this case the flammable aerosol cloud is formed by smouldering combustion in a confined space such that low volatility, flammable aerosol is released. The aerosol cloud is liable to ignite suddenly. This type of explosion is therefore a particular hazard to fire fighters. One such incident occurred in a warehouse fire at Chatham dockyard involved smouldering mattresses, and two men were killed. The phenomenon is sometimes known as a 'Chatham matress' fire.

17.30.2 Crankcase explosions

The work of Burgoyne and co-investigators on the combustion of flammable mists and spray, described in Chapter 16, was undertaken in large part in relation to the problem of mist explosions in crankcases. This has been investigated by Burgoyne, Newitt and Thomas (1954) and by Burgoyne and Newitt (1955).

Crankcase explosions are relatively rare, but a marine crankcase explosion in 1947, which claimed 28 lives, showed that a serious hazard existed and led to the initiation of research.

The suspension of oil in air in an engine crankcase during normal running is a mechanical spray with some condensed mist from the lubricated parts which are at temperatures above the average in the crankcase. If there is serious overheating, however, condensed mist formation is accelerated, a condition often referred to as 'smoke'.

Measures which may be taken to avoid a crankcase explosion are ventilation to keep the atmosphere below the lower flammability limit, or injection of inert gas to suppress flammability, and explosion relief. The design of the latter requires a knowledge of the burning velocity.

As described earlier, the work on condensed oil mists demonstrated that these have flammability characteristics similar to those of the mixture given by the same amount of substance wholly in vapour form at the somewhat higher temperature necessary for vaporization. The lower flammability limit was 0.049 g/l. Flammability was suppressed when the air contained 28.3% of carbon dioxide.

It is now usual to fit crankcases with explosion relief devices.

17.30.3 Superheated liquid explosions: explosions in plant

A liquid may become superheated in various ways. It may be heated while under hydrostatic pressure or it may be heated in a boiling regime which favours superheating. The superheat energy may then be released.

Normally superheat is released without great violence by the generation of nucleated bubbles. This occurs, for example, in normal heat transfer to a boiling liquid.

In some cases the release of vapour is rather more violent. A layer of water at the bottom of the tank of hot oil, for example, may become superheated so that there is a sudden evolution of vapour.

It has been suggested by R. King (1975a–c, 1976a,b, 1977, 1990) that such an occurrence may have contributed to the Flixborough disaster. The temporary 20 in. pipe was installed between reactors No. 4 and 6. Reactor No. 4 was fitted with an agitator, but this had not been in use for some time. It is possible that in the absence of agitation a layer of water may have built up in the bottom of the reactor and, on being heated up during start-up, may have caused a sudden evolution of vapour sufficient to rupture the pipe assembly.

Another type of superheat explosion can occur when a refrigerated liquid hydrocarbon mixture such as LNG is poured on to water. This type of explosion is considered in Section 17.29.7.

17.30.4 Air system explosions

Explosions in compressed air system have been reported over the years in coal mines and, more recently, in the process industries also. An explosion in a compressed air line in Germany in 1963 killed 19 people.

Accounts of the explosion hazard in compressed air systems have been given by Mallow (1964a,b), Fowle (1973) and Burgoyne and Craven (1973).

Characteristically, a compressed air system explosion occurs on the air line from a reciprocating compressor with oil lubricated cylinders. Often the compressor has a record of faulty operation and of high outlet temperature prior to the explosion. Carbonaceous residues are frequently found just downstream of the compressor outlet.

Explosions in compressed air systems are essentially oil mist explosions. The thickness of the oil film capable of giving a flammable mist is given by Burgoyne and Craven as follows:

$$t = \frac{CDP}{4d} \qquad [17.30.1]$$

where C is the mass of oil mist in air necessary to produce an explosive mixture at atmospheric pressure (g/m^3), d is the density of the oil (g/m^3), D is the diameter of the pipe (m), P is the absolute pressure (atm) and t is the thickness of the oil film (m). The minimum value of C is the lower flammability limit, which for hydrocarbons in general is about $49\,g/m^3$, but work by Loison (1952) indicates that the practical value is about $138\,g/m^3$, which is about 2.8 times the theoretical value.

If this oil film is dispersed into an oil mist by some primary shock or explosion, the conditions are created for a more powerful secondary explosion. High outlet temperatures (>250°C) of the compressed air can vaporize and ignite the oil. Sudden release of high pressure can cause simultaneous mist formation and ignition. Carbonaceous residues can undergo self-heating and give ignition.

It should be emphasized that fires are more common than explosions in compressed air systems, but the fire creates an explosion hazard.

The oil film explosion which occurs in a compressed air line with a thin film of flammable oil is somewhat unique. Typically the air line is ruptured at intervals over its length. The explosion is a detonation, but its nature is not entirely understood. The problem has been discussed by Burgoyne and Craven.

A number of oil film explosions have occurred in the compressed air starter systems of large diesel engines. In these cases, the explosion generally appears to have been initiated by the diesel engine rather than by the air compressor.

There are a number of measures which can be taken to prevent air system explosions. One is to use oils which are non-flammable or have reduced flammability. The oils available and the problems associated with their use are discussed by Burgoyne and Craven.

It is usually suggested that the risk of explosion can be reduced if high oil usage is avoided. This is not a complete answer, however, as explosions have occurred in systems where oil usage was not abnormally high.

The deposition of oil can be minimized by the design of the air compressor. The air velocity in the outlet pipe should be high, although a velocity which might cause vibration should be avoided. The air flow in the aftercooler should be downwards so that it is in the same direction as the oil film flow. There should be drain points so that oil can be removed from the system.

In operating the compressor, particular attention should be paid to the air outlet temperature. Various authors have suggested outlet temperature limits in the region of 140–150°C.

In Germany the maximum air outlet temperature of air compressors is determined by law. The maximum temperature was set at 160°C in 1934, but explosions continued to occur. In 1963 it was reduced to 140°C.

It has been suggested by Burgoyne and Craven, however, that for pressures above 10 atm this may still not be the safe working temperature. They recommend a maximum normal working temperature of 145°C for a final stage outlet pressure of 10 atm gauge, but one of 124°C for a pressure of 100 atm gauge, with automatic cut-off temperatures 10°C higher in both cases. A more detailed table of values is given by these authors.

It is also important for there to be a high standard of maintenance both of the air compressor and also of the rest of the air system.

Other detailed precautions are described by the authors quoted.

17.30.5 Molten metal–water explosions

A violent explosion can occur if water comes into contact with molten metal. This hazard is of particular concern in the nuclear and metallurgical industries, but may sometimes occur in the process industries.

Molten metal–water explosions can occur either where water is added to molten metal or where molten metal is added to water.

There are a number of theories of molten metal–water explosions, including theories of superheat not unlike those described in Section 17.29.7, but the phenomenon is not well understood.

An investigation of molten metal–water explosions with special reference to continuous casting is given in *A Study of the Causes of Molten Metal and Water Explosions* by the HSE (1977/18). This report describes the various theories of such explosions.

A molten–metal water explosion was the cause of the Scunthorpe disaster in 1975 in which a large leak of water from the cooling water pipe ran down into a torpedo ladle of molten iron (Case History A78).

17.30.6 Superheated liquid explosions: explosions on water

As mentioned above, one form of superheated liquid explosion is that occurring inside plant. Another is that which can occur when a refrigerated liquefied hydrocarbon is spilled onto water.

Accounts of this type of explosion have been given by Katz and co-workers (Katz and Sliepcevich, 1971; Katz, 1972), R.P. Anderson and Armstrong (1972, 1974), Enger and Hartman (1972a,b) and Reid, Drake and co-workers (Drake, Jeje and Reid, 1975; Reid, 1976, 1978; Drake and Reid, 1977; Reid and Smith, 1978).

Attention was drawn to the potential for such an explosion during work on the hazards associated with the transport of LNG and involving its spillage on to water at the Bureau of Mines (BM) (Burgess, Murphy and Zabetakis, 1970 BM S 4105; Burgess, Biordi and Murphy, 1972 BM PMSRC 4177). In the 56th test of an otherwise uneventful series, a sharp explosion destroyed the experimental water tank. Later, a similar but larger explosion was experienced when $0.25\,m^3$ of LNG was spilled on a pond in the open.

Explosions of this kind are variously known as physical vapour explosions, flameless vapour explosions, or simply vapour explosions, and as rapid phase transition (RPT) explosions.

A theory to explain such explosions is given by Reid (1976). The explosion is a form of superheated liquid explosion and is governed by the superheat limit temperature. An explosion of this kind can occur in a BLEVE, and the phenomenon is considered as an aspect of BLEVE in Section 17.29. As stated there, Reid's expression for the superheat limit temperature (SLT) is

$$T_{sl} = 0.895T_c \qquad [17.30.2]$$

where T_c is the critical temperature (K) and T_{sl} is the superheat limit temperature (K). If a liquid is heated above its SLT, rapid vapour bubble nucleation occurs followed by an explosive evolution of vapour.

According to this theory, spillage of a cold liquid on to a hotter one can result in a superheat limit explosion. As the BM work indicates, this occurs only in a proportion of cases.

The limiting conditions for occurrence of an SLT are discussed by Reid with reference to those for propane. The SLT of propane is 326 K (53°C). The range of water temperatures within which vapour explosions of propane of any violence occur is 326–344 K. Below 326 K the water temperature is less than the SLT of propane whilst above 344 K the phenomenon appears to be suppressed by the boiling regime.

For small temperature differences the heat transfer regime is nucleate boiling, but as the temperature difference increases film boiling takes over. The heat transfer in this latter regime is reduced so that the cold liquid then has only a thin film above the SLT. Limited to this thin film, the violence of the SLT explosion is much less.

Thus, although liquefied gases such as ethane and methane have lower SLTs, they do not in their pure form give vapour explosions.

The same applies to LNG which is essentially pure methane. However, it is found that if an LNG contains a sufficient proportion of higher hydrocarbons a vapour explosion can occur. A vapour explosion is thus a credible event.

The proportion of higher hydrocarbons in an LNG which would not undergo a vapour explosion may be increased by ageing or by differential vaporization of the methane to the point where it would.

The initial vapour explosion may be followed by a more violent one; the primary explosion may result in further contacting of the cold and hot liquids due to the pressure wave and to droplet formation.

Several groups of workers have reported research on the industrial aspect of the hazard from such explosions. In addition to the BM work they include R.P. Anderson and Armstrong (1972, 1974) and Enger and Hartman (1972a,b).

Enger and Hartman consider particularly the situation where LNG is subject to depletion of the methane content to the point where a vapour explosion is possible. They point out that in these circumstances the weathering is likely to be uneven so that any given instant an explosion would occur only at part of the interface.

These workers estimate the mechanical energy release as some $0.5\,cal/m^2$ of interface area.

The consensus view which appears to have emerged is that such vapour explosions are not a prime cause of concern.

17.31 Effects of Explosions

An explosion may give rise to the following effects: (1) blast damage, (2) thermal effects, (3) missile damage, (4) ground shock, (5) crater and (6) injury.

Not all these effects are given by every explosion. An aerial blast, for example, tends not to form a crater.

Many of the data on the effects of explosions come, not surprisingly, from studies of military and industrial explosives, but an increasing amount of information is available from the investigation of process plant explosions.

Information on the effects of explosions has been given in *Explosions, Their Anatomy and Destructiveness* (C.S. Robinson, 1944), *Structural Defence* (Christopherson, 1946), the *Textbook of Air Armaments* (Ministry of Supply, 1952), *The Effects of Nuclear Weapons* (Glasstone, 1962; Glasstone and Dolan, 1980), *Hazards of Chemical Rockets and Propellants* (Jensen, 1972),

Workbook for Predicting Pressure Waves and Fragment Effects of Exploding Propellant Tanks and Gas Storage Vessels (W.E. Baker *et al.*, 1975), *Handbook for Estimating the Effects of Accidental Explosions in Propellant Handling Systems* (W.E. Baker *et al.*, 1978), *Explosion Hazard and Evaluation* (W.E. Baker *et al.*, 1983), *Methods for the Determination of Possible Damage to People and Objects Resulting from Releases of Hazardous Materials* (the *Green Book*); (CPD, 1992b), and by Jarrett (1968), Brasie and Simpson (1968), V.J. Clancey (1972b), Eisenberg, Lynch and Breeding (1975) and Gilbert, Lees and Scilly (1994a–i).

Selected references on the effects of explosions are given in Table 17.38.

Table 17.38 *Selected references on effects of explosions*

Blast effects, blast theory, blast scaling laws
MOD, ESTC (n.d.); Hugoniot (1887–89); Christopherson (1944, 1946); C.S. Robinson (1944); Sachs (1944); E. Fisher (1950, 1953a,b); Los Alamos Scientific Laboratories (1950); von Neumann and Richtmyer (1950); Weibull (1950); Prentiss (1951); Goldstein and von Neumann (1953); Brode (1955, 1957, 1959); Hoffman and Mills (1956); Hoerner (1958); Shear and Day (1959); Ericsson and Edin (1960); Goodman (1960); Shear and McCane (1960); Glasstone (1962); Kinney (1962); Langefors and Kihlstrom (1963–); Kingery and Pannill (1964); Office of Civil Defense (1965); Wistoski and Snyer (1965); Keefer *et al.* (1966); Kingery (1966); Brasie and Simpson (1968); Callahan (1968); E. Cohen (1968); Dobbs, Cohen and Weissman (1968); Jarrett (1968); D.L. Jones (1968, 1970); Masso and Rudd (1968); Petes (1968); Stagg and Zienkiewicsz (1968); Teller *et al.* (1968); Lehto and Larson (1969); Penney, Samuels and Scorgie (1970); Stephens (1970); Zimmer, McDevitt and Dale (1970); Woolfolk (1971); Anon. (1972e); V.J. Clancey (1972b, 1982); Jensen (1972); Pittman (1972a,b, 1976); Westine (1972, 1977); W.E. Baker (1973); J.W. Reed (1973); Rindner and Wachtel (1973); Woolfolk and Ablow (1973); Geiger (1974); W.G. High (1974, 1976); W.E. Baker *et al.* (1975); Eisenberg, Lynch and Breeding (1975); K. Kaplan, Gabrielsen and von Horn (1975); Strehlow and Baker (1975, 1976); Swisdak (1975); Reissler, Pettit and Kennedy (1976, 1977); Strehlow and Ricker (1976); W.E. Baker *et al.* (1978); M.R. Baum (1979); Department of Energy (USA) (1980); Glasstone and Dolan (1980); Zeeuwen and Schippers (1980); W.E. Baker *et al.* (1983); Held (1983a,b); Hannum (1984); Kingery and Bulmash (1984); Dowding (1985); Kinney and Graham (1985); MHAP (1986 LPB 68, 1989); Cruice (1986); Dangreaux (1986); Esparza (1986); F.G. Bell (1987); van Loo and Opschoor (1989); P.A. Davies (1993)
Explosions in confined spaces: W.I. Taylor (1968); Weibull (1968); Stretch (1969); Slack (1971); Lazari, Burley and Al-Hasani (1991)
(see also Table 17.13)
Vapour cloud explosions: J.H.S. Lee (1977); A.F. Roberts and Pritchard (1982); S.F. Hall *et al.* (1982); Zeeuwen, van Wingerden and Dauwe (1983); Giesbrecht (1988); Pritchard (1989); C.J.M. van Wingerden, van den Berg and Opschoor (1989); Guibert *et al.* (1992); CCPS (1994/15)

Effect of blast on structures
Ministry of Home Security (Appendix 28, n.d.b); Philip (1945); Christopherson (1946, 1949); R.F. Meyer (1957); Healy (1959); Stretch (1969); Alexander and Hambly (1970); F. Morton (1970); Slack (1971); Wiehle and Bockholt (1971); Mainstone (1972); Alexander and Taylor (1973a,b); ASCE (1974/3, 1985/21, 1986/26); Westine and Baker (1974); FRS (1976 Fire Res. Note 1054); W.E. Baker *et al.* (1983); Jowett (1984 SRD R295); D.M. Brown and Nolan (1985, 1987); Cruice (1986); Jowett and Byrne (1986 SRD R376); Jowett, Byrne and Roberts (1986 SRD R377); Scilly and High (1986); Weerheijm (1988); US Army, Navy and Air Force (1990); Mercx, Weerheijm and Verhagen (1991); Opschoor, van Loo and Pasman (1992); van Wees and Mercx (1992); Whitney, Barker and Spivey (1992); Barker, Whitney and Waclawczyk (1993)
Brickwork: Astbury *et al.* (1970); Sinha and Hendry (1970); Paterson and Rowe (1970); Hendry and Sinha (1971); Hendry, Sinha and Maurenbrecher (1971); J. Morton, Davies and Hendry (1971); Astbury and Vaughan (1972); Astbury, West and Hodgkinson (1972, 1973); J. Morton and Hendry (1973); H.W.H. West, Hodgkinson and Webb (1973); Beak *et al.* (1994)

Blast resistant structures
Samuely and Hamann (1939); Christopherson (1946); J.F. Baker, Williams and Lax (1948); Earthquake Engineering Research Institute (1952); Newmark (1956a,b); Porter *et al.* (1956); Loving (1957); US Army, Corps of Engineers (1957); Norris *et al.* (1959); Browne *et al.* (1961); Rebenstorf (1961); Weber *et al.* (1961); Glasstone (1962); Kinney (1962); R.G. Rose and Howell (1962); ASCE (1963); J.B. Martin and Symonds (1966); AIA (1967); W.G. High (1967, 1974); C.V. Moore (1967); E. Cohen (1968); E. Cohen and Dobbs (1968a,b); Dobbs, Cohen and Weissman (1968); H.G. Johnston (1968); R.Y. Levine (1968a); Ruyters (1968); Sewell and Kinney (1968); Department of the Army, the Navy and the Air Force (1969); Alexander and Hambley (1970); Allgood and Swihart (1970); Recht (1971); C.E. Reynolds (1971); Granstrom (1972); Whitman (1973); W.E. Lawrence and Johnson (1974); Westine and Baker (1974); B.G. Cox and Saville (1975); Langeveld (1976); Balemans and van de Putte (1977); D.K. Pritchard (1981, 1983, 1989); Forbes (1982); Pritchard (1983); Tunkel (1983); D.M. Brown and Nolan (1985, 1987); Nolan and Brown (1986); Power and Krier (1986); Bailly *et al.* (1989); D.M. Brown (1986).
Vapour cloud explosions: Geiger (1987)

Effect of blast on plant and equipment
J.R. Wilson (1968); F.E. Walker (1969); M.M. Stephens (1970, 1973); Pickering and Bockholt (1971); Weldon (1972); Hymes (1984); D.M. Brown and Nolan (1985, 1987); Nolan and Brown (1986); Dangreaux (1986); Scilly and High (1986); Verheij (1988)

Missiles, including generation, characteristics and flight
Didion (1860); Helie (1884); Petry (1910); Cranz and Becker (1921); Cranz (1926); Gurney (1943, 1946); Christopherson (1946); Anon. (1951); I.G. Bowen, Strehler and Wetherbe (1956); J.N. Nielsen (1960); Synge and Griffiths (1960); I.G. Bowen, Albright *et al.* (1961); E. R. Fletcher, Albright *et al.* (1961); Shapiro

(1961); I.G. Bowen *et al.* (1963a,b); Grodzovksy and Kukanov (1965); E.R. Fletcher and Bowen (1968); Gwaltney (1968); Rindner (1968); R.C. Smith and Smith (1968); B. Brown (1969); D.E. Taylor and Price (1971); Zaker (1971, 1975a,b); Pittman (1972a,b, 1976); W.E. Baker, Cox *et al.* (1973); Bessey (1974); W.E. Baker *et al.* (1975); Clancy (1975); Bessey and Kulesz (1976); Ardron, Baum and Lee (1977); W.E. Baker, Westine and Cox (1977); Westine (1977); W.E. Baker *et al.* (1978); W.E. Baker, Cox *et al.* (1978); HSE (1978b); SIPRI (1978); M.R. Baum (1979, 1984, 1988, 1989, 1991, 1993); J.H. Bowen (1980); Munday (1980); Porter (1980); Tulacz and Smith (1980); W.E. Baker *et al.* (1983); Holden and Reeves (1985); Hunt and Wood (1985 SRD R341); Pietersen (1985); Hart and Croft (1988); McCleskey (1988a,b, 1992); Naz (1989); de Mestre (1990); M.C. Miller (1990); Pineau *et al.* (1991); Scilly and Crowther (1992); Twisdale and Vickery (1992); Twisdale *et al.* (1992); CCPS (1994/15)

Missiles from craters: Henny and Carlson (1968)

Missile impact and impact effects

NDRC (1946); Duwez, Clark and Bohnenblast (1950); Parkes (1955); Loving (1957); Ezra (1958); Zabel (1958); Goldsmith (1960); Kolsky (1963); R.W. White and Botsford (1963); Cottrell and Savolainen (1965); C.V. Moore (1967); E.R. Fletcher, Bowen and Perret (1965); Gwaltney (1968); Symonds (1968); Kinslow (1970); Calder and Goldsmith (1971); A.J. Morris and Calladine (1971); W. Johnson (1972); W.G. High (1974, 1980); Linderman (1974); B.G. Cox and Saville (1975); N. Jones (1976, 1983); R.P. Kennedy (1976); Berriaud *et al.* (1978); HSE (1978b) SIPRI (1978); Barr *et al.* (1980); Bokor (1980); J.H. Bowen (1980); I.L. Davies (1980); Hopkirk, Lympany and Marti (1980); A.J. Neilson (1980); Porter (1980); Porter *et al.* (1980); Tulacz and Smith (1980); Woisin (1982); W.E. Baker *et al.* (1983); Hunt and Wood (1985 SRD R341); ASME (1986 PVP 106, 1989/173); Jowett (1986 SRD R378); Wierzbicki and Myung Sung Suh (1986); Barr (1987 SRD R439); Ciolek (1988); Vazques-Sierra, Marti and Molina (1988); Lu (1989); A.C. Palmer (1989); Scilly and Crowther (1992)

Windows, glass fragments

Beckett (1937, 1958); Preston (1942); C.S. Robinson (1944); T.C. Baker and Preston (1946); N.J. Thompson and Cousins (1949); Charles (1958); Iverson (1968); J.W. Reed *et al.* (1968); Mainstone (1971); E.R. Fletcher, Richmond and Jones (1973, 1976); H.W.H. West (1973); E.R. Fletcher (1974); E.R. Fletcher and Richmond (1974); Eisenberg, Lynch and Breeding. (1975); E.R. Fletcher, Richmond and Richmond (1974); Ministry of Social Affairs (1976); M.R. Marshall, Harris and Moppett (1977); Harvey (1979b); E.R. Fletcher, Richmond and Yelverton (1974); J.W. Reed (1980, 1992); Pritchard (1981); W.E. Baker *et al.* (1983); Dangreaux (1986); Harmanny and Opschoor (1986); Scilly and High (1986); CPD (1992a,b)

Effect of explosions on people, explosion injury

Ministry of Home Security (Appendix 28); Zuckerman (1940, 1941a,b); Blocker (1949); Blocker and Blocker (1949); Surgeon General (1950); Ministry of Supply (1952); C.S. White (1963, 1965, 1968a,b, 1971, 1974); C.S. White, Bowen and Richmond (1964); E. Cohen (1968); von Gierke (1968); A.E. Hirsch (1968); R.K. Jones and Richmond (1968); Richmond, Damon *et al.* (1968); Department of the Army (1969); Richmond and Fletcher (1971); Fugelso, Weiner and Schiffman (1972); E.R. Fletcher, Bowen *et al.* (1972); E.R. Fletcher, Richmond and White (1974); Eisenberg, Lynch and Breeding. (1975); Fricke (1975); W.E. Baker *et al.* (1978); HSE (1978b, 1981a); V.C. Marshall (1978); Crawley (1982); Hymes (1984); Cruice (1986); Dangreaux (1986); Hadjipavlou and Carr-Hill (1986); MHAP (1986 LPB 68, 1989); Withers (1988); Mercx (1990); Pineau *et al.* (1991); Withers and Lees (1991); CPD (1992b); Opschoor, van Loo and Pasman (1992); Sorenson, Carnes and Rogers (1992); Gilbert, Lees and Scilly (1994a–i)

Direct blast effects – lung haemorrhage: Zuckerman (1940, 1941); O'Reilly and Gloyne (1941); Stewart, Russel and Cone (1941); Krohn, Whitteridge and Zuckerman (1942); Clemedson (1956); Richmond, Taborelli *et al.* (1957); Richmond, Wetherbe *et al.* (1957); C.S. White (1959, 1961); C.S. White and Richmond (1959, 1960); Richmond, Clare *et al.* (1961); Richmond and White (1962a,b); C.S. White, Bowen and Richmond (1965); Betz *et al.* (1965); Damon *et al.* (1966); I.G. Bowen, Fletcher and Richmond (1968); I.G. Bowen, Fletcher *et al.* (1968); Damon *et al.* (1968); Richmond, Damon *et al.* (1968); E.R. Fletcher and Richmond (1971); C.S. White, Jones *et al.* (1971); E.R. Fletcher, Bowen *et al.* (1972); C.S. White, Jones *et al.* (1972); Coppell (1976); Rawlins (1977–78); Stapczynski (1982); Y.Y. Phillips (1986); Zheng (1990)

Direct blast effects – eardrum rupture: Zalewski (1906); Vadala (1930); Blake *et al.* (1941); Zuckerman (1941); G.A. Henry (1945); F.G. Hirsch (1968); Reider (1968); C.S. White, Bowen and Richmond (1970); Kerr and Byrne (1975a,b)

Bodily translation, tumbling: Gurdjian, Webster and Lissner (1949); Taborelli and Bowen (1957); Taborelli, Bowen and Fletcher (1959); Swearingen *et al.* (1960); I.G. Bowen, Woodworth *et al.* (1962); I.G. Bowen, Fletcher and Perret (1965); E.R. Fletcher and Bowen (1968); A.E. Hirsch (1968); E.R. Fletcher and Richmond (1970); E.R. Fletcher, Richmond and Jones (1971a,b); E.R. Fletcher, Richmond *et al.* (1971); Richmond (1974); E.R. Fletcher, Yelverton *et al.* (1975); R.K. Jones, Richmond and Fletcher (1975)

Injury by building debris: Bowles *et al.* (1991); Gilbert, Lees and Scilly (1994h)

Crushing: Burzstein (1989)

Injury by missiles, wound ballistics

Bircher (1899); Journée (1907); Gurney (1944); Grundfest *et al.* (1945); Anon. (1947); Andrus *et al.* (1948); Harvey (1948); Goldizen, Richmond and Chiffelle (1957); Goldizen *et al.* (1961); Beyer (1962); French and Callender (1962); A. Palmer (1962); Sperraza and Kokinakis (1967, 1968); Clemedson, Hellstrom and Lindgren (1968); Mattoo, Wani and Askegar (1974); R.C. Gray and Coppell (1975); Zaker (1975a,b); di Maio (1981); di Maio *et al.* (1982); Neades and Rudolph (1983); Trunkey (1983); J.H. Lewis *et al.* (1987); McCleskey, Needes and Rudolph (1990); Timberwolf Consulting Services (1991); Gilbert, Lees and Scilly (1994f–i)

Injury by flying glass

R.C. Bell (1944); I.G. Bowen, Richmond *et al.* (1956); Sperrazza and Kokanis (1967, 1968); E.R. Fletcher

(1974); E.R. Fletcher and Richmond (1974); E.R. Fletcher, Richmond and Yelverton (1980); W.E. Baker *et al.* (1983); Connell (1983, 1992); Gilbert, Scilly and Lees (1994h)

Injury inside buildings
C.S. White (1957); Department of the Army, the Navy and the Air Force (1969); Richmond (1971, 1972); Richmond and Kilgore (1971); Fricke (1975); Withers and Lees (1991); Hewkin (1992); Gilbert, Lees and Scilly (1994a–d,h,i)
Dust injury, asphyxiation: Ministry of Supply (1952); C.S. White (1957)
Crush injury: Michaelson, Taitelman and Burstein (1984); Michaelson *et al.* (1984); Ron *et al.* (1984); Burstein (1989)

Combined injuries
R.K. Jones (1971); Schildt (1972); CPD (1992b); Gilbert, Lees and Scilly (1994h)

Injury by weapons, including wartime air raids and terrorist bombs
Anon. (n.d.b); Blake and Douglas (n.d.); Lyons and Gardner (n.d.a–c); Zuckerman (1940, 1941); Payne (1941); Osborn (1943); R.C. Bell (1944); Commissioner of Police (1945); Public Record Office (1945a–e); Anon. (1946); Howgrave-Graham (1947); Dunn (1952); Ministry of Supply (1952); Home Office (1953); O'Brien (1955); Collier (1957); Healy (1959); Irving (1963); MacNalty and Mellor (1968); Blocker *et al.* (1969); Mellor (1972); Rutherford (1972–73); Caro and Irving (1973); Ramsey (1974, 1983, 1987); Fricke (1975); R.C. Gray and Coppell (1975); T.L. Kennedy and Johnson (1975); Tucker and Lettin (1975); Waterworth and Carr (1975); J. Reed (1977); Sainsbury (1977); Lord Baker (1978); Hadden, Rutherford and Merett (1978); J.F. Hill (1979); Longmate (1981, 1985); Brismar and Bergenwald (1982); R.V. Jones (1982); Pyper and Graham (1982–83); G.J. Cooper *et al.* (1983); Rely (1987); Fryckberg and Tepas (1988); Patience (1989); Neville (1990); Moran (1992)

17.31.1 Blast damage

One of the principal effects of an explosion is the creation of a blast wave, and much of the energy of the explosion is expended on this.

A description of blast effects must take into account both the nature of the blast wave and the damage caused by the blast to structures. The energy entering the blast wave was considered in Section 17.4 and the characteristics of the blast wave in Section 17.25 and its damage effects are described in Sections 17.32 and 17.33.

17.31.2 Missile damage

Another principal effect of an explosion is the generation of missiles, and this takes up most of the energy not transmitted to the blast wave.

A description of missile damage involves both the generation and flight of missiles and the damage caused by missiles to structures. The energy imparted to missiles was considered in Section 17.4 and the generation and flight of missiles and the damage done by them is described in Sections 17.34 and 17.35.

17.31.3 Thermal effects

The combustion process involved in a chemical explosion can give rise to intense local heat radiation, which may cause damage or injury.

Information on the effects of thermal radiation in explosions, mostly derived from nuclear explosions, was given in Chapter 16.

17.31.4 Ground shock

In industrial explosions ground shock effects are usually small and less than those due to blast and assessment of such effects is generally not undertaken.

The effects of ground shock may, however, furnish useful information in accident investigation. An account of ground shock in this context has been given by V.J. Clancey (1972b).

The ground shock produced by an explosion may be regarded as a sinusoidal disturbance and may be characterized by its frequency and amplitude and thus also by its maximum velocity and maximum acceleration:

$$V_{\max} = 2\pi f A \qquad [17.31.1]$$

$$a_{\max} = 4\pi^2 f^2 A \qquad [17.31.2]$$

where a is the acceleration, A is the amplitude, f is the frequency, V is the velocity and the subscript 'max' denotes the maximum value.

For a charge exploded at the ground surface the ground shock depends mainly on the quantity of explosive and the nature of the ground.

An equation widely used to determine the amplitude of ground shock is

$$A = 0.001\frac{KE^{\frac{1}{2}}}{d} \qquad [17.31.3]$$

where A is the amplitude (in.), d is the distance (ft), E is the mass of explosive (lb) and K is a constant. The constant K depends on the nature of the ground. It may be taken as 100 for hard rocks and 300 for clay.

In order to avoid damage to a building owned by others, the amplitude should be limited to a value of 0.008 in. for an average structure or 0.003 in. for a delicate one. The persons responsible for the blast hazard may, however, opt to take the risk of some damage to their own building and allow an amplitude of 0.016 in.

For comparison, an amplitude of 0.001 in. is detectable by someone who is on the lookout for a tremor and one of 0.003 in. may be produced by heavy traffic nearby.

The frequency of the ground shock may be as low as 3–5 Hz in soft or loose soil and as high as 30–100 Hz in rock.

The damage done by ground shock to normal houses has been correlated by Langefors and Kihlstrom (1963) in terms of the quantity

$$\phi = \frac{Q}{R^{\frac{3}{2}}} \qquad [17.31.4]$$

where Q is the mass of explosive (kg) and R is the distance (m).

Some data on damage to normal houses caused by ground shock are given by Langefors and Kihlstrom for hard rock, and further derived data are given by Clancey for soft rock, as shown in Table 17.39. The relationship

Table 17.39 *Some data on damage to normal houses by ground shock*

(*Data in this table from* Rock Blasting *by U. Langefors and B. Kihlstrom, 1963, are reproduced with permission of the authors and of the publishers, Almqvist & Wiksell Forlag*)

$Q/R^{\frac{3}{2}}$		*Damage to normal houses*
Hard rock ($kg/m^{\frac{3}{2}}$)	*Soft rock* ($kg/m^{\frac{3}{2}}$)	
0.008	0.02	Fall of plaster, no cracking
0.06	0.25	Insignificant cracking (threshold value)
0.12	0.50	Cracking
0.25	1.0	Major cracking

Sources: Hard rock: Langefors and Kihlstrom (1963). Soft rock: Clancey (1972b).

is not valid for distances less than 2–3 times the depth at which the explosion takes place. The values given are for damage to normal houses built on the rock in which the explosion occurs. For concrete structures the f value needed to give the same degree of damage is 2–4 times greater.

For an explosion at or near the surface damage by blast will extend to a much greater distance than damage by ground shock.

17.31.5 Crater

A condensed phase explosion tends to give rise to a crater. For industrial explosions this effect is not usually assessed beforehand, but may provide information useful in accident investigation.

Accounts of cratering are given by C.S. Robinson (1944) and by V.J. Clancey (1972b, 1977d).

The factors which affect the crater produced by an explosion are the position of the charge relative to the ground surface, the nature of the ground, and the type and quantity of explosive. A charge exploded at the ground surface gives a wider and shallower crater than one exploded just beneath the surface.

The crater is larger in rock than in soft sand. In the latter there is very little shock transmission; in the former, however, the initial shock propagates and produces cracks as the pressure wave passes. The expanding gases enter the cracks and accelerate the fragmented rock.

It may be noted that understanding of the effects of the nature of the soil on crater size has developed over the years and the effects just outlined differ from those described by Robinson.

A high brisance explosive generally gives a large crater, and a low brisance explosive a small one or none at all. Vapour cloud explosions tend not to give craters; there was no crater at Flixborough.

An equation for crater size which applies to the explosion of dynamite, a high brisance explosive, at the ground surface on average soil is the Olsen formula

$$V = 0.4Q^{\frac{8}{7}} \qquad [17.31.5]$$

where Q is the mass of explosive (lb) and V is the volume of the crater (ft^3).

Robinson gives the experimental data on crater size shown in Table 17.40. The third case is the explosion at Oppau in 1921 (Case History A5). The corresponding crater volumes calculated from Equation 17.31.5 are 3200 and 75 000 000 ft^3, respectively. Thus the low brisance ammonium nitrate gave a crater size considerably smaller than that calculated by the equation derived for the high brisance explosive.

An equation relating the diameter of a crater to its volume has been given by V.C. Marshall (1987). He obtains from Robinson's figures the relation

$$D = 3\frac{V^{0.5}}{h} \qquad [17.31.6]$$

where D is the diameter of the crater (m), h is its depth (m) and V is its volume (m^3). Then utilizing the rule-of-thumb attributed by Robinson to Olsen that the height of the crater is on average half its diameter ($h = D/2$) he gives

$$D = 6V^{0.25} \qquad [17.31.7]$$

Assuming that crater volume is proportional to the cube of the radius, Equation 17.31.5 is broadly consistent with the other main relation used to describe crater dimensions

$$r \propto W^{\frac{1}{3}} \qquad [17.31.8]$$

where r is the radius of the crater and W the mass of explosive.

As mentioned in Section 17.3, there is a reasonably good correlation between the crater radius and the mean detonation distance for ground surface explosions, so that relation 17.31.8 is similar to Equations 17.3.5 and 17.3.6.

Cratering can occur even without an explosion. The V-2 rockets, which had very high kinetic energy, were capable of giving a large crater even when not armed.

17.31.6 Injury

The effects of an explosion on people include injury caused by (1) blast, (2) missiles, (3) thermal effects and (4) toxic effects. These injury effects are described in Sections 17.38 and 17.39.

Table 17.40 *Crater dimensions (after C.S. Robinson, 1944)*

Explosive		*Crater dimensions*		
Type	*Charge* (lb)	*Diameter* (ft)	*Height* (ft)	*Volume* (ft^3)
Dynamite	50	6	2	30
Dynamite	2 400	31	9	3 200
Ammonium nitrate	9000 000	400	90	10 000 000

17.32 Explosion Damage to Structures

17.32.1 Air blast loading

The general nature of the air blast from an explosion has been discussed in Section 17.25, where the blast characteristics were described essentially in terms of an ideal condensed phase explosion such as that of TNT, while the differences in the blast between a condensed phase explosion and a vapour cloud explosion were considered in Sections 17.26 and 17.28.

The loading of structures by air blast is described by Glasstone (1962) and Glasstone and Dolan (1980). In general, the effective pressure p_e on a given face of a structure is the sum of the overpressure p and of the drag pressure p_d:

$$p_e(t) = p(t) + p_d(t) \qquad [17.32.1]$$

The drag pressure p_d is a function of the dynamic pressure q:

$$p_d(t) = C_D q(t) \qquad [17.32.2]$$

where C_D is the drag coefficient.

Glasstone and Dolan treat various structures, including (1) a closed, box-like structure, (2) a partially open, box-like structure, (3) an open frame structure, (4) a cylindrical structure and (5) an arched structure.

For the case of a closed, box-like structure, it is possible to determine (1) the average front face loading, (2) the average side and top loading, (3) the average back face loading and (4) the net horizontal loading.

If a blast wave reaches the structure and its incidence on the front face is normal, the overpressure p_f at that face rises very rapidly to the peak reflected overpressure p_r^o. As the wave moves around the structure, the front face pressure falls rapidly to the stagnation pressure p_s at the stagnation time t_s,

$$p_f = p_s = p(t_s) + p_d(t_s) \qquad [17.32.3a]$$

$$= p(t_s) + q(t_s) \qquad [17.32.3b]$$

since for this face C_D is unity. The stagnation time

$$t_s = 3S/U \qquad [17.32.4]$$

where S is the distance through which pressure relief is obtained and U is the shock velocity. S is the height H or the half-breadth $B/2$, whichever is the smaller.

Thereafter the front face pressure falls:

$$p_f = p(t) + q(t) \qquad [17.32.5]$$

The front face pressure is shown in Figure 17.83(a).

The average side face and top pressure is obtained from Equations 17.32.1 and 17.32.2 as follows. The side face is fully loaded when $t = L/U$, where L is the structure length, and at this time the average pressure reaches a maximum value p_a corresponding to that at $t = L/2U$. Thereafter the average pressure is that corresponding to $t - L/2U$, until it falls to zero at $t = t_d + L/2U$. The drag coefficient is approximately -0.4. The average side face and top pressure is shown in Figure 17.83(b).

The average back face pressure is obtained from Equations 17.32.1 and 17.32.2 as follows. The shock front reaches the back face at time $t = L/U$, but it requires an additional time of $4S/U$ for the average pressure to build up to the maximum value p_b corresponding to that at $t = (L + 4S)/U$. Thereafter the average pressure is that corresponding to $t - L/U$, until it falls to zero at $t = t_d + L/U$. The drag coefficient is approximately -0.3. The average back face pressure is shown in Figure 17.83(c).

The net horizontal loading is the front face loading less the back face loading. This is shown in Figure 17.84.

The response of the walls is depends primarily on the loadings on the individual faces, while the response of the frame depends on the net loading.

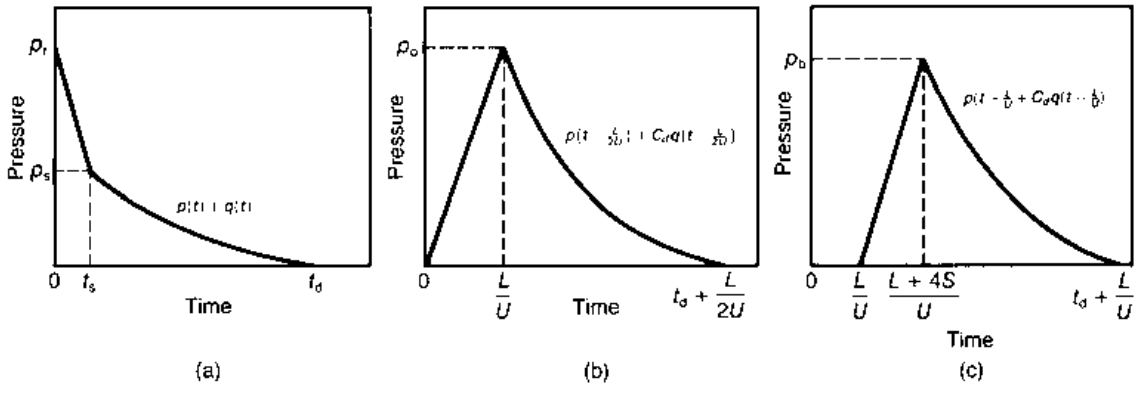


Figure 17.83 *Blast loading of structures – average pressure loading on a closed cuboid structure (Glasstone and Dolan, 1980): (a) average front face loading; (b) average side and top loading; and (c) average back face loading (Courtesy of Castle House Publications)*

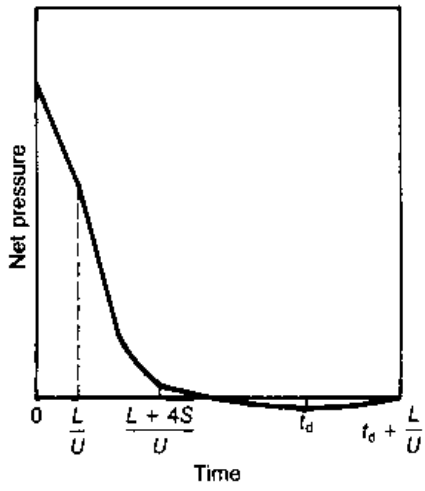


Figure 17.84 *Blast loading of structures – net pressure loading on a closed cuboid structure (Glasstone and Dolan, 1980): net horizontal loading (Courtesy of Castle House Publications)*

For the shock strengths of interest here the values required for the drag coefficient C_D are those applicable to the subsonic range. Some values of the drag coefficient are given in Table 17.41.

17.32.2 Diffraction and drag loading

In the air blast loading of structures a distinction is made between diffraction loading and drag loading. Diffraction loading is determined primarily by the peak overpressure, drag loading by the dynamic, and hence the drag, pressure.

There are two types of diffraction loading. One is that due the pressure differential between the front and back faces. Except for long structures this load is short-lived. The other loading is that due to the pressure differential between the inside and outside of the building. This approximates a static load and is more prolonged. With diffraction loading the damage potential is a function of the peak overpressure and the duration.

Drag loading is due to the drag pressure on the structure.

The loading is a function both of the air blast and the structure. A given structure may display diffraction or drag type behaviour, depending on the duration. A short duration tends to load by diffraction, a long one by drag.

For a closed structure the duration of diffraction loading is approximately the time for the wave to pass from front to back, which is a relatively short period. Drag loading exists for the whole duration of the positive phase and for a short time thereafter. This is a long period compared with that of diffraction loading.

Certain types of structure are more prone to damage by diffraction, others by drag. Diffraction type targets tend to be closed or semi-closed structures such as buildings with small window areas and storage tanks. Drag type targets tend to be tall, thin objects such as telegraph poles and lamp posts. Buildings with large window areas may also constitute drag-type targets.

Drag loading is relatively more important for explosions which give long duration times, such as nuclear explosions, than for those giving short duration times, such as TNT.

17.32.3 Structure response

A typical load–displacement diagram is illustrated in Figure 17.85(a) and other related diagrams are shown in Figures 17.85(b)–(d).

The response of a structure is usually modelled by treating it as a lumped system. The simplest model is the one-mass model. The one-mass system is illustrated in Figure 17.86(a). The general equation of motion is

$$m\frac{d^2x}{dt^2} + c\frac{dx}{dt} + R(x) = F(t) \qquad [17.32.6]$$

where c is the damping factor, F is the applied force, m is the mass, R is the restoring force, t is the time and x is the displacement. It is usual to assume zero damping. Hence Equation 17.32.6 becomes

$$m\frac{d^2x}{dt^2} + R(x) = F(t) \qquad [17.32.7]$$

For a system in the elastic regime the retarding force R is proportional to the displacement x. Hence Equation 17.32.6 becomes

$$m\frac{d^2x}{dt^2} + c\frac{dx}{dt} + kx = F(t) \qquad [17.32.8]$$

Or neglecting damping, as illustrated in Figure 17.86(b)

$$m\frac{d^2x}{dt^2} + kx = F(t) \qquad [17.32.9]$$

where k is the elastic constant.

For a system in the plastic regime the retarding force is the Coulomb friction, or retarding, force f. Hence, as illustrated in Figure 17.86(c), Equation 17.32.9 becomes

$$m\frac{d^2x}{dt^2} + f = F(t) \qquad [17.32.10]$$

In this case motion occurs only if $F > f$.

Considering first the one-mass vibrator, shown in Figure 17.86(a), the equation of motion may be written as

$$\tau^2\frac{d^2x}{dt^2} + 2\zeta\tau\frac{dx}{dt} + x = F^* \qquad [17.32.11a]$$

$$\frac{1}{\omega_n^2}\frac{d^2x}{dt^2} + \frac{2\zeta}{\omega_n}\frac{dx}{dt} + x = F^* \qquad [17.32.11b]$$

with

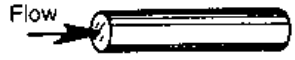
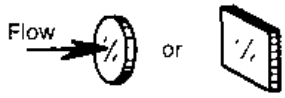
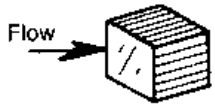
$$F^* = F/k \qquad [17.32.12]$$

$$\tau = \left(\frac{m}{k}\right)^{\frac{1}{2}} \qquad [17.32.13]$$

$$\omega_n = \left(\frac{k}{m}\right)^{\frac{1}{2}} \qquad [17.32.14]$$

$$\zeta = \left(\frac{c^2}{4mk}\right)^{\frac{1}{2}} \qquad [17.32.15]$$

Table 17.41 *Drag coefficients (W.E. Baker et al., 1983; after Hoener, 1958)*

Shape	*Sketch*	C_D
Right Circular Cylinder (long rod), side-on		1.20
Sphere		0.47
Rod, end-on		0.82
Disc, face-on		1.17
Cube, face-on		1.05
Cube, edge-on		0.80
Long Rectangular Member, face-on		2.05
Long Rectangular Member, edge-on		1.55
Narrow Strip, face-on		1.98

where ζ is the damping factor, τ the natural period and ω_n the natural frequency.

If there is no damping, the one-mass vibrator becomes an elastic oscillator, as shown in Figure 17.86(b). The behaviour of the elastic oscillator gives important insight into the response of structures. If the system is subject to an applied force which decays exponentially such that

$$F(t) = F \exp(-t/T) \qquad [17.32.16]$$

where T is the time constant of the decay of the force, Equation 17.32.9 becomes

$$m\frac{d^2x}{dt^2} + kx = F \exp(-t/T) \qquad [17.32.17]$$

The general solution of Equation 17.32.17 is

$$\frac{x}{F/k} = f(\omega_n t,\ \omega_n T) \qquad [17.32.18]$$

and the solution x_m for maximum values of x is

$$\frac{x_m}{F/k} = f(\omega_n T) \qquad [17.32.19]$$

where $x_m/(F/k)$ is the amplification factor and $\omega_n T$ the duration ratio. The relation between these two quantities

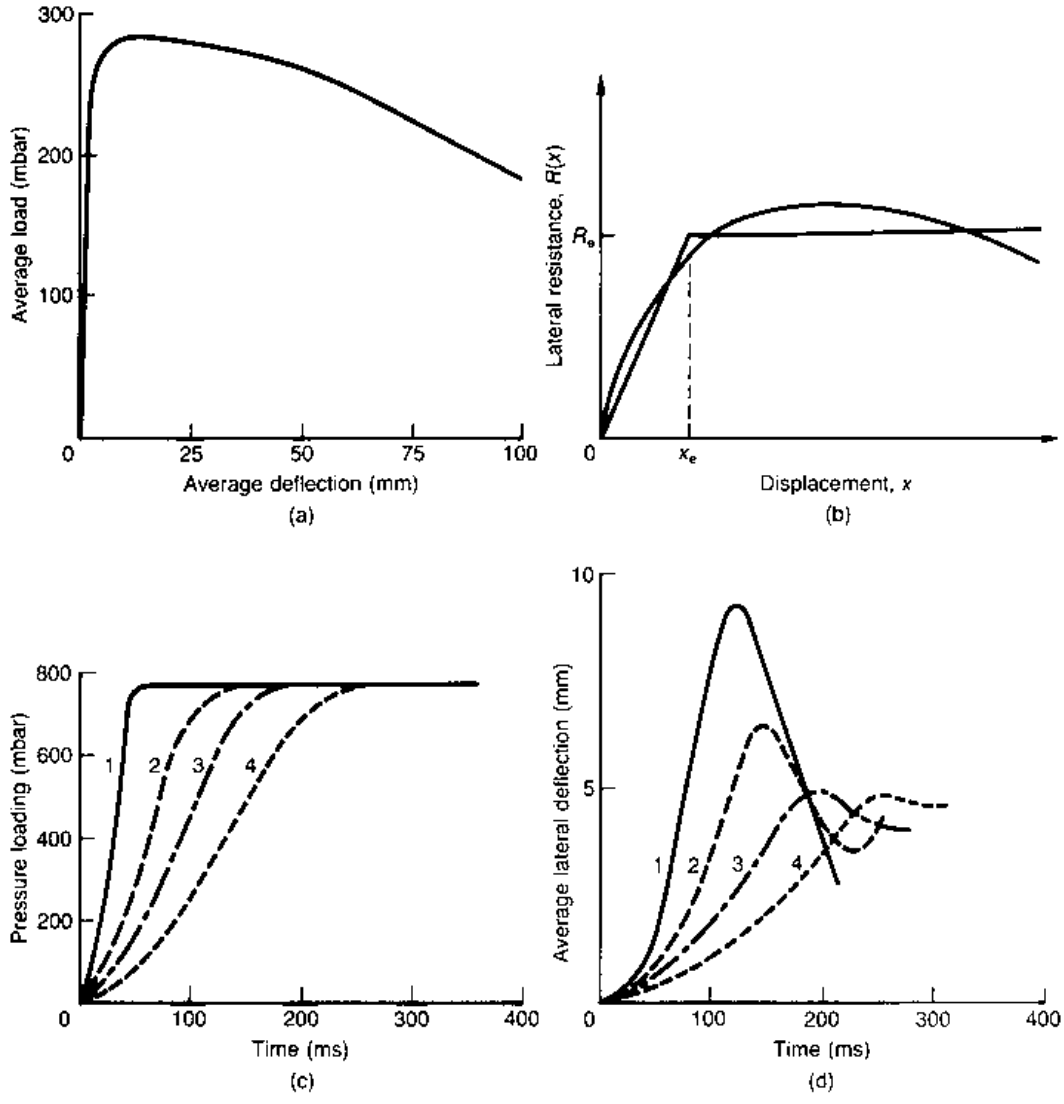


Figure 17.85 *Blast loading of structures: load–displacement and related diagrams: (a) load–displacement diagram; (b) resistance–displacement diagram; (c) load–time diagram; and (d) displacement–time diagram. 1–4, rise times*

is given in the oscillator diagram shown in Figure 17.87. The asymptotes of the curve given in Figure 17.87 are

$$\frac{x_m}{F/k} = \left(\frac{k}{m}\right)^{\frac{1}{2}} T = \omega_n T \qquad \omega_n T < 0.4 \qquad \text{Impulsive loading} \qquad [17.32.20a]$$

$$= 2 \qquad \omega_n T > 40 \qquad \text{Quasi-static loading} \qquad [17.32.20b]$$

$$= f(\omega_n T) \qquad 0.4 < \omega_n T < 40 \qquad \text{Dynamic loading} \qquad [17.32.20c]$$

In sketching the curve it is also helpful to note that at the value of $\omega_n T$ where the asymptotes intersect the value of $x_m/(F/k)$ on the actual curve is approximately half that at the point of intersection. Then in the impulsive loading domain

$$x_m \propto FT = I \qquad [17.32.21]$$

where I is the impulse, whilst in the quasi-static loading domain

$$x_m = 2F/k \qquad [17.32.22]$$

Equation 17.32.22 means that the dynamic displacement, or deflection, is twice the static displacement. This

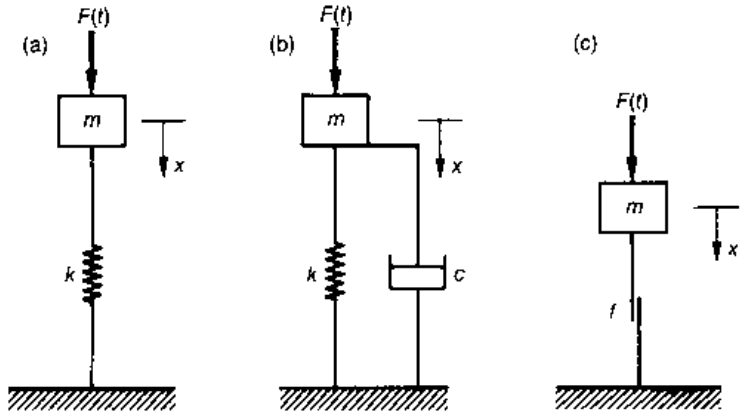


Figure 17.86 *Blast loading of structures – one-mass representation of a structure: (a) undamped elastic spring system (linear oscillator); (b) damped elastic spring system (viscous damping); and (c) rigid-plastic system (Coulomb friction)*

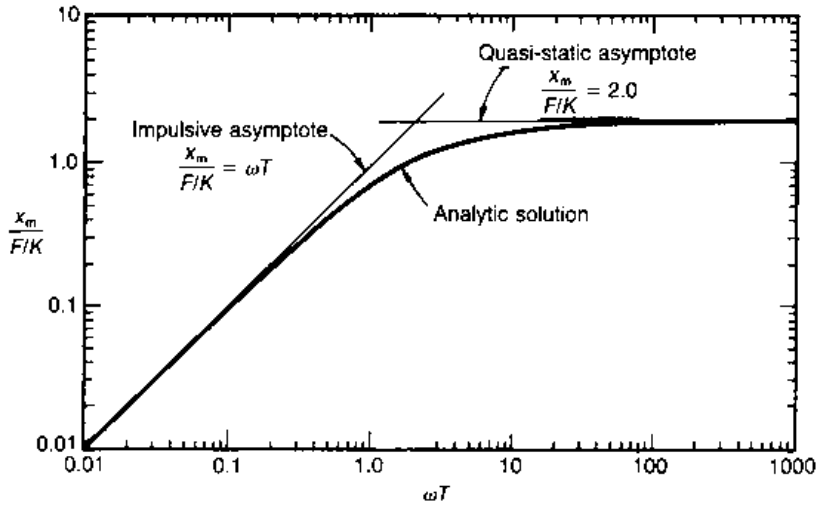


Figure 17.87 *Blast loading of structures: response of an elastic structure (after W.E. Baker et al., 1983) (Courtesy of Elsevier Science Publishers)*

dynamic load factor of 2 is widely used in structural engineering.

It is also of interest to consider the corresponding energy relations. For impulsive loading the maximum strain energy may be equated with the initial kinetic energy. The initial velocity is

$$\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{t=0} = \frac{I}{m} \qquad [17.32.23]$$

and the initial kinetic energy E_{ko} is

$$E_{\mathrm{ko}} = \frac{m}{2}\left(\frac{I}{m}\right)^2 = \frac{I^2}{2m} \qquad [17.32.24]$$

The maximum strain energy E_{sm} is

$$E_{\mathrm{sm}} = \frac{1}{2}kx_{\mathrm{m}}^2 \qquad [17.32.25]$$

Equating the two energies to obtain the asymptote

$$\frac{I}{(km)^{\frac{1}{2}}x_{\mathrm{m}}} = 1 \qquad [17.32.26]$$

Similarly, for quasi-static loading the maximum strain energy may be equated with the maximum work W_{m}. The latter is

$$W_{\mathrm{m}} = Fx_{\mathrm{m}} \qquad [17.32.27]$$

Equating the two energies

$$\frac{2F}{kx_m} = 1 \qquad [17.32.28]$$

as in Equation 17.32.22.

These relationships may be represented graphically in the form of a force–impulse, or *F–I*, diagram, as illustrated in Figure 17.88, which shows again the three domains of impulsive loading and quasi-static loading separated by dynamic loading.

The force–impulse diagram is readily converted to a pressure–impulse, or *P–I* diagram, as described below.

A similar treatment may be applied to the plastic regime. In this case the maximum strain energy is

$$E_{sm} = fx_m \qquad [17.32.29]$$

Equating energies as before gives

$$\frac{F}{f} = 1 \qquad [17.32.30]$$

$$\frac{I}{(2mfx_m)^{\frac{1}{2}}} = 1 \qquad [17.32.31]$$

There are also more complex multiple-mass models of structural response.

An account of the practical application of these concepts to the buildings typical of chemical plants has been given by Whitney, Barker and Spivey (1992). The work included investigations of the structural damage in a number of plant accidents and covered peak reflected overpressures of 0.1–15 psi and duration of 5–100 ms. The authors distinguish three types of blast load: impulsive, quasi-static and dynamic. They classify the loads as low, moderate and high, defined in terms of the combination of peak overpressure and duration. They then tabulate for each load class the typical damage to frames, purlins, girts and joists, metal decking, and windows, and they indicate the level of protection afforded by the structure and make recommendations for design.

The response of buildings to blast is generally analysed using a static load of long duration. The authors state that the metal frame buildings common in chemical plant tend to have greater impulsive and dynamic resistance than the static analysis indicates. It is quite common for plant buildings to experience a dynamic response in which the duration of the load is close to the natural period of the structure. The conventional plant buildings which perform best are those which allow plastic response without failure. The thrust of the design recommendations is to enhance this plastic behaviour.

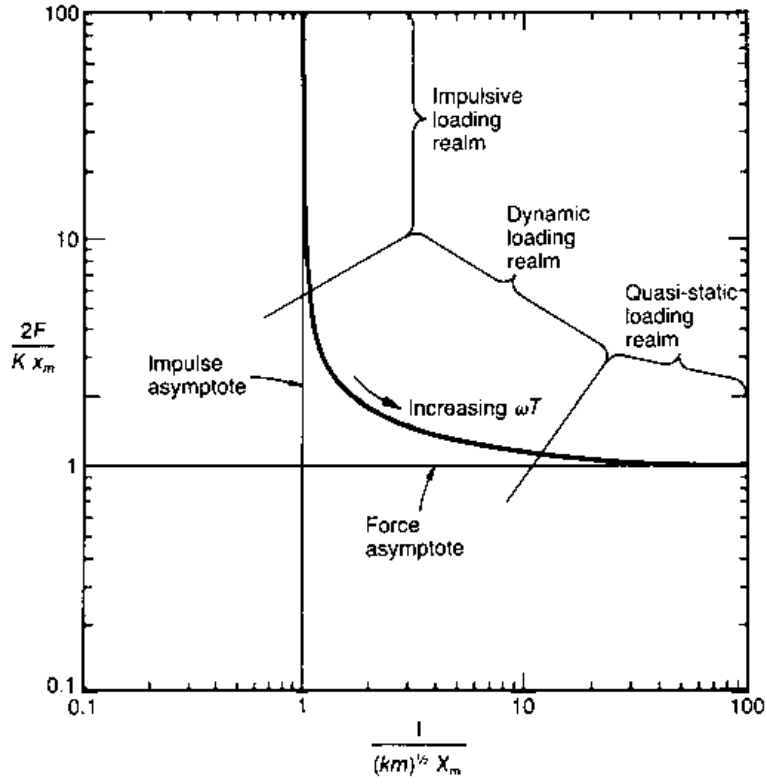


Figure 17.88 *Blast loading of structures: force–impulse (F–I) diagram of a structure (Strehlow and Baker, 1976) (Reprinted from R.A. Strehlow and W.E. Baker,* Progress in Energy and Combustion Science*, 2, 27, Copyright © 1976, with permission from Pergamon Press)*

17.32.4 Structure parameters

Some parameters which govern the structure response are (1) the natural period, (2) the elastic limit, (3) the ductility ratio and (4) the resistance function.

The elastic behaviour of a structure may be described in terms of the following parameters:

$$T_n = 1/f_n \quad [17.32.32]$$

$$= 2\pi/\omega_n \quad [17.32.33]$$

$$= 2\pi(m/k)^{\frac{1}{2}} \quad [17.32.34]$$

where f_n is the natural cyclic frequency, T_n the natural period and ω_n the natural frequency.

Equation 17.32.34 may be used to determine the elastic constant from the natural period, and vice-versa. Some typical values of the natural period given by R.J. Harris (1983) are

Brick walls 20–40 s

Concrete walls 10–15 s

Concrete floors 10–30 s

A table of equations for the determination of the natural period is given by W.E. Baker *et al.* (1983). The following empirical equation is given by Kinney (1962) for the estimation of the natural period of a reasonably modern building:

$$T = 0.05\frac{H}{B^{\frac{1}{2}}} \quad [17.32.35]$$

where B is the breadth of the building (ft), H is its height (ft) and T is its natural period (s).

The extent of elastic behaviour is determined by the elastic limit, which is essentially the limit for a static load. Information on the elastic limit is available for most materials of interest. For structural response, where the time of application of the load may be very short, the relevant limit may be the dynamic elastic limit. Some approximate data on the elastic limit for structural materials have been given by Kinney (1962). According to these data the ratio of the dynamic to the static resistance for structural steel is about 1.58 up to a time to yield of 5.5 ms and that for reinforced concrete is about 1.38 up to a time to yield of 10 ms. For both materials the ratio falls to about 1.15 at a time to yield of 100 ms.

Kinney states that the time to reach the maximum elastic displacement, or time to yield t_e, has been investigated using the equation of motion, and may be approximately represented by the relation

$$t_e = \frac{T}{4}\left(\frac{p_m}{r_e}\right)^{-\frac{1}{2}} \quad [17.32.36]$$

where p_m is the blast pressure (N/m^2), r_e is the maximum elastic resistance per unit area (N/m^2), t_e is the time to yield (s) and T is the natural period (s).

The ductility ratio μ is the ratio of the total sustainable deformation to the elastic deformation:

$$\mu = \frac{x_f}{x_e} \quad [17.32.37]$$

where x_e is the displacement at the elastic limit and x_f is that at the failure limit. A material with a low ductility ratio is brittle, one with a high ratio ductile.

The behaviour of a structure under load is given by the load–displacement curve, which was illustrated in Figure 17.85(a). If this curve is treated as a resistance-displacement curve, the resistance function R may be obtained from it by approximating the curve by two straight lines, as shown in Figure 17.85(b). At the maximum elastic displacement x_e there is a maximum elastic resistance R_e, or yield resistance.

17.32.5 Component failure

The behaviour of a structural component may be illustrated by considering that of a brick wall. Work on the response of load-bearing brick structures to gas explosions has been described by Astbury *et al.* (1970), and their report contains an appendix by Paterson and Rowe (1970) on experimental work on the dynamic loading of brick panels.

Figure 17.89 shows the load–displacement diagram for brick panels of varying thickness. There is a rise to a maximum load F_m with a given central deflection x_m. The load decays to zero at a failure deflection x_f. These three parameters are functions of the bricks, the mortar, the panel thickness, the aspect ratio and the edge-fixing conditions. The failure deflection x_f is usually somewhat more than the panel thickness. From other work the ratio of central to average deflection is taken as 1 : 0.44.

From experimental work several simple rules have been derived for scaling load–deflection curves. It is found that if the linear dimensions of a panel are altered by a uniform scaling factor, the lateral strength remains constant. It is also found that the strength is proportional

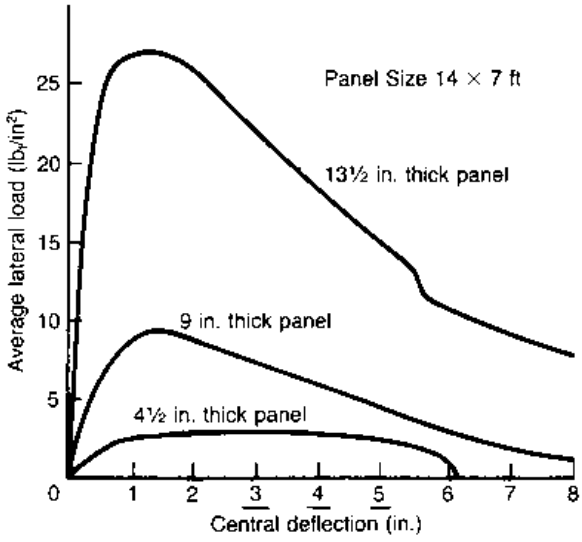


Figure 17.89 *Blast loading of structures: load–displacement diagram for brick panels (after Astbury et al., 1970) (Courtesy of the British Ceramics Research Association)*

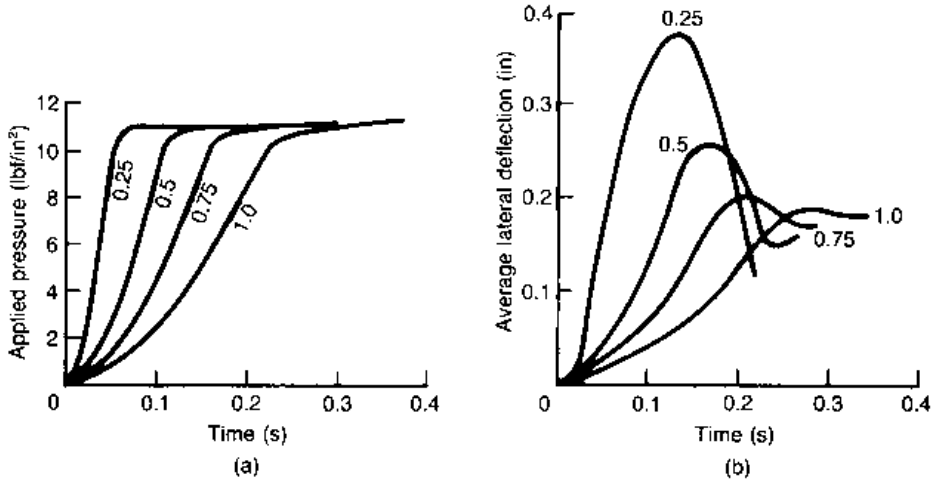


Figure 17.90 *Blast loading of structures – effect of rapidly applied loads on a 9 in. brick wall (after Astbury et al., 1970): (a) applied load; (b) average lateral deflection. Curve parameters on both figures are fractions of longest rise time 200 ms. (Courtesy of the British Ceramics Research Association)*

to the square of the thickness. Further, comparing a square with a rectangle comprising two such squares, it is found that the strength of the latter is half that of the former, that for intermediate values of the aspect ratio it is possible to interpolate and that for greater values the strength remains constant at the value for the rectangle.

Although the elasticity of brickwork is very limited, for rapidly applied loads the dynamic strength is somewhat greater than the static strength. In other words, there is some increase in maximum deflection with increase in rate of pressure rise. This is illustrated for a 9 in. brick wall in Figure 17.90.

There is a marked increase in dynamic deflection as the failure loading is approached. This is illustrated for a 4.5 in. brick wall in Figure 17.91, which shows that at explosions with maximum pressure P_m of 4 $lb_f/in.^2$ the deflection is slight, but that at a pressure of 4.2 $lb_f/in.^2$ there is a large deflection, failure finally occurring at 5.1 $lb_f/in.^2$.

Some information is available on the failure pressures of building components. Tables are given by Astbury *et al.* (1970) and by R.J. Harris (1983).

17.32.6 Overpressure damage data

Structural damage caused by blast waves from explosions has traditionally been correlated in terms of the peak overpressure of the explosion. There are available a large number of tables and graphs giving damage levels in terms of the peak overpressure.

The applicability of such data is greater for quasi-static loading than it is for impulsive loading. In the latter regime this approach is liable to result in considerable overestimate of the damage.

Thus, W.E. Baker *et al.* (1983) recommend against the use of simple overpressure damage data. Preferred methods are the use of pressure impulse, or *P–I*, diagrams and distance–charge, or *R–W* correlations.

However, useable data in these alternative forms are often not available. In addition, some refinement of the overpressure approach has been effected. It still appears worthwhile, therefore, to consider first this approach.

A survey of damage effects caused by accidental explosions has been made by C.S. Robinson (1944), who also gives graphs of the limits of serious damage, of minor damage, of glass breakage and of missile flight versus charge for both barricaded and unbarricaded installations. The data given by Robinson for unbarricaded installations are plotted in Figure 17.92.

A large amount of information on blast damage is given by Glasstone (1962) and Glasstone and Dolan (1980). These include buildings of various kinds, gas works, oil storage tanks, LPG installations, electrical transmission systems, and gas, water and sewage systems, and vehicles and ships. These data are based mainly on blast caused at Hiroshima and Nagasaki by the explosion of a nuclear bomb of approximately 20 000 t TNT equivalent over each city in 1945 and by tests conducted at the Nevada Test Site, supplemented by data from accidental explosions.

Some of the damage effects described by Glasstone are as follows. In the Texas City explosion in 1947, oil storage tanks were severely damaged out to the overpressure region of 3–4 psi.

In the Nevada tests in 1955 a complete 18 000 US gal bulk storage plant containing propane with pump, compressor, piping, valves and fittings, and with a cylinder filling building, was located at the point where the overpressure was 5 psi. The building was demolished and the filling line was broken at the point where it entered the building, but otherwise the installation received only superficial damage.

In the Nagasaki explosion in 1945 the water supply system suffered extensive damage, so that it became virtually impossible to extinguish fires. Breakage of pipes occurred almost entirely in or at the entrance to buildings and structures rather than underground. The exception was a 12 in. cast iron water main 3 ft below

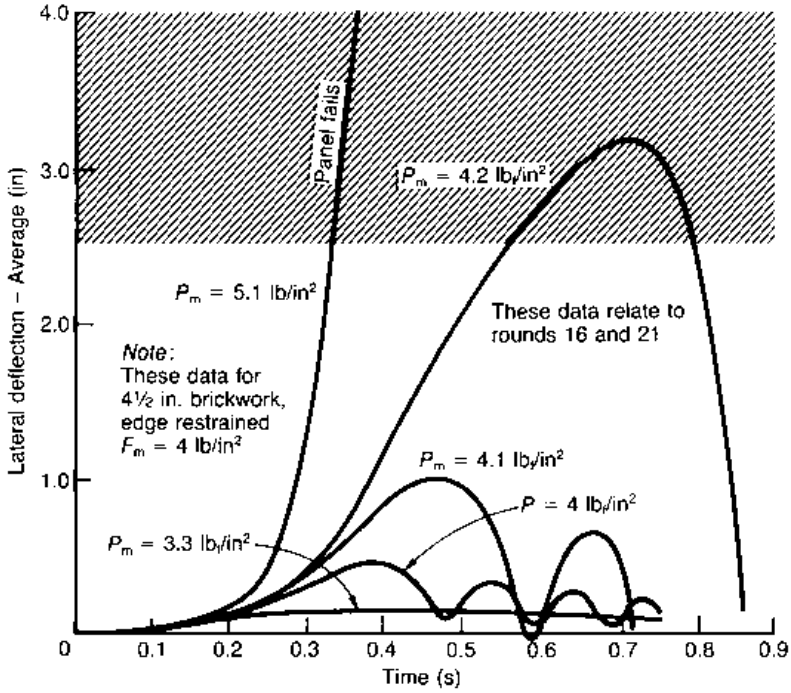


Figure 17.91 *Blast loading of structures: effect of rapidly applied loads on a 4.5 in. brick wall as failure loading is approached (after Astbury et al., 1970) F_m ultimate strength; P_m, maximum explosion pressure (Courtesy of the British Ceramics Research Association)*

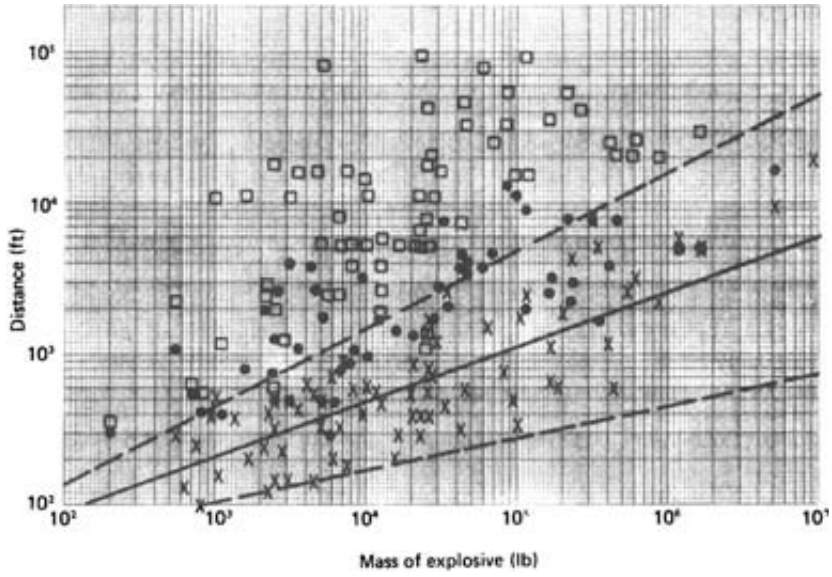


Figure 17.92 *Damage effects of explosions: limits of serious damage, missile flight and glass damage for accidental explosions for unbarricaded installations (after C.S. Robinson, 1944): ×, severe damage; ●, missile flight; □, glass breakage. The full and broken lines give, respectively, the average and the outer limits for serious damage (Reproduced with permission from* Explosions: their Anatomy and Destructiveness *by C.S. Robinson, Copyright © 1944, McGraw-Hill Book Company)*

Table 17.42 *Some damage effects produced by a blast wave – 1 (after Glasstone, 1962; Brasie and Simpson, 1968)*

A Original data of Glasstone[a]

Structural element	*Failure*	*Peak side-on overpressure (approximate)* (psi)
Glass windows, large and small	Shattering usually, occasionally frame failure	0.5–1.0
Corrugated asbestos siding	Shattering	1.0–2.0
Corrugated steel or asbestos panelling	Connection failure followed by buckling	1.0–2.0
Brick wall panel, 8 or 12 in. thick, not reinforced	Shearing and flexure failures	3.0–10.0 (7–8)
Wood siding panels, standard house construction	Usually failure occurs at the main connections, allowing a whole panel to be blown in	1.0–2.0
Concrete or cinder-block wall panels, 8 or 12 in. thick, not reinforced	Shattering of the wall	1.5–5.5 (2–3)

B Additional data of Brasie and Simpson[b]

Structural element	*Failure*	*Peak side-on overpressure (approximate)* (psi)
Self-framing steel panel building	Collapse	3–4
Oil storage tanks	Rupture	3–4
Wooden utility poles	Snapping failure	5
Loaded rail cars	Overturning	7

[a] Glasstone and Dolan (1980), Table 5.145. Values in brackets from Brasie and Simpson (1968).
[b] Brasie and Simpson (1968), Table 3.

ground which did break, but this was in a filled area where the ground was irregular. There appeared to have been little effect on underground gas mains.

Glasstone gives a large amount of data on levels of damage to both diffraction- and drag-type structures, including a number of tables and nomograms. In particular, the data shown in Table 17.42 have been widely quoted. The data given in section A of the table are from an original table of Glasstone. Those given in section B are quoted together with the data from section A by Brasie and Simpson (1968), and are possibly taken from the text of Glasstone. The table given by Brasie and Simpson has frequently been quoted.

Another damage table is that given by V.J. Clancey (1972b) in the context of accident investigation and reproduced in Table 17.43.

Commenting on these tables, Scilly and High (1986) state that both the tables of Brasie and Simpson and that of Clancey are largely derived from the nuclear weapons data and theoretical analyses in Glasstone together with some additional data for condensed phase explosives from Robinson.

Table 17.43 *Some damage effects produced by a blast wave – 2 (after V.J. Clancey, 1972b)*

	Peak side-on overpressure	
	(psi)	(kPa[a])
Annoying noise (137 dB), if of low frequency (1–15 Hz)	0.02	
Occasional breaking of large glass windows already under strain	0.03	0.2
Loud noise (143 dB). Sonic boom glass failure	0.04	
Breakage of windows, small, under strain	0.1	0.7
Typical pressure for glass failure	0.15	1.0
'Safe distance' (probability 0.95 no serious damage beyond this value)	0.3	2.0
Missile limit		
Some damage to house ceilings; 10% window glass broken		
Limited minor structural damage	0.4	2.8
Large and small windows usually shattered; occasional damage to window frames	0.5–1.0	3.5–6.9
Minor damage to house structures	0.7	4.8
Partial demolition of houses, made uninhabitable	1.0	6.9
Corrugated asbestos shattered	1–2	6.9–13.8
Corrugated steel or aluminium panels, fastenings fail, followed by buckling		
Wood panels (standard housing), fastenings fail, panels blown in		
Steel frame of clad building slightly distorted	1.3	9.0
Partial collapse of walls and roofs of houses	2	13.8
Concrete or cinder block walls, not reinforced, shattered	2–3	13.8–20.7
Lower limit of serious structural damage	2.3	15.9
50% destruction of brickwork of house	2.5	17.3
Heavy machines (3000 lb) in industrial building suffer little damage	3	20.7
Steel frame building distorted and pulled away from foundations		
Frameless, self-framing steel panel building demolished	3–4	20.7–27.6
Rupture of oil storage tanks		
Cladding of light industrial buildings ruptured	4	27.6
Wooden utilities poles (telegraph, etc.) snapped	5	34.5
Tall hydraulic press (40 000 lb) in building slightly damaged		
Nearly complete destruction of houses	5–7	34.5–48.3
Loaded train wagons overturned	7	48.3
Brick panels, 8–12 in. thick, not reinforced, fail by shearing or flexure	7–8	48.3–55.2
Loaded train boxcars completely demolished	9	62.1
Probable total destruction of buildings	10	69.0
Heavy (7000 lb) machine tools moved and badly damaged		
Very heavy (12 000 lb) machine tools survived		
Limit of crater lip	300	2000

[a] These SI values are given by Gugan (1979).

A damage classification which is widely quoted is that by Stephens (1970), who defines the following categories:

Zone	*Damage level*	*Peak side-on overpressure* (kPa)
A	Total destruction	>83
B	Severe damage	>35
C	Moderate damage	>17
D	Light damage	<3.5

The damage levels typical of these zones are such that in A the building may be damaged beyond economical repair, in B it suffers partial collapse and/or failure of some structural members, in C it is still usable but structural repairs are required, and in D damage includes broken windows, light cracks in walls and damage to wall panels and roofs.

Fugelso, Weiner and Schiffman have described damage to frame structures from an explosion equivalent of 500 t TNT equivalent. The following data have been quoted in the vulnerability model by Eisenberg, Lynch and Breeding (1975) from this work:

Structural damage (%)	*Peak overpressure*	
	(psi)	(N/m^2)
1 (threshold)	0.9	6 200
50	3.0	20 700
99	5.0	34 500

They derive from these data a probit equation relating structural damage to peak overpressure:

$$Y = -23.8 + 2.92 \ln p^{o} \qquad [17.32.38]$$

where p^{o} is the peak overpressure (N/m^2) and Y is the probit.

In further development of the vulnerability model, Rausch, Eisenberg and Lynch (1977), have dealt with the disintegration of walls and the resultant flying debris. Rausch, Tsao and Rowley (1977) review explosion damage to various types of structure, including frame structures, low office blocks and warehouses. They also give data from Pickering and Bockholt (1971) on explosion damage to process storage such as floating roof tanks, vertical pressure vessels and spherical tanks. The damage levels are quoted at 20% (structural damage) and 99% (total destruction):

Damage level (%)	*Peak overpressure* (psi)	(N/m^2)
Steel floating roof petroleum tank		
20	3.5	24 132
99	20.0	137 895
Vertical cylindrical steel pressure vessel		
20	12.0	82 737
99	14.0	96 527
Spherical steel petroleum tank		
20	8.0	55 158
99	16.0	110 316

A description of the effects of the overpressure in the Flixborough explosion has been given by Sadee, Samuels and O'Brien (1976–77). Among the installations at Flixborough were some storage tanks which were situated about 250 m from the epicentre of the explosion and were severely damaged. It is estimated in the First *Canvey Report* (HSE, 1978b) that, assuming an explosion equivalent to 20–30 t of TNT, the tanks would have been subjected to an overpressure of about 0.1 bar. This overpressure for tank failure is used in the report.

A further account of overpressure damage to various items of plant and transport equipment is given in the study by Gugan (1979).

There is a considerable amount of other data on the effect of air blast on buildings. An overpressure of 1 psi is sufficient to cause partial demolition, whilst one of 10 psi usually causes total destruction.

Table 17.44 is another damage table, given by Scilly and High (1986) for use in estimating damage for explosions with yields in the range 1–100 te TNT equivalent. The preferred approach of these authors is use of *R–W* or *P–I* methods, but the table is given for use where data in those forms are not available. The provision of separate data for explosions of different size makes some allowance for factors other than overpressure.

A further damage table is given by the CCPS (1994/15).

17.32.7 *R–W* correlations

An approach to the correlation of structural damage from blast waves now increasingly preferred is the use of a distance–charge, or *R–W*, correlation. Discussions of the

Table 17.44 *Some damage effects produced by a blast wave – 3 (Scilly and High, 1986) (Courtesy of the Societe de Chimie Industrielle; reproduced with permission)*

Structural element	*Failure mode*	*Peak side-on overpressure*[a] *(approximate)* (psi)		
		Explosive charge		
		1 te	10 te	100 te
Window frames	5% broken	0.15	0.1	0.1
	50% broken	0.36	0.24	0.21
	90% broken	0.9	0.6	0.54
Houses	Tiles displaced	0.64	0.42	0.38
	Doors and window frames frames may be blown in	1.3	0.86	0.77
	Category D damage	0.71	0.44	0.42
	Category Ca damage	1.8	1.15	1.10
	Category Cb damage	4.0	2.4	2.3
	Category B damage	11.5	5.2	5.0
	Category A damage	26.5	11.5	11.0
Telegraph poles	Snapped	52	26	24
Large trees	Destroyed	57	26	24
Primary missiles	Limit of travel	0.2	0.14	0.12
Rail wagons	Limit of derailment	26.5	11.5	11.0
	Bodywork crushed	20	8.7	8.4
	Damaged but easily repairable	11.5	5.7	5.5
	Superficial damage	4.6	2.6	2.5
Railway line	Limit of destruction	205	97	93

[a] All distances (and equivalent overpressures) are measured to the furthest point of the structure from the explosion source.

use of the *R–W* method are given by W.E. Baker *et al.* (1983) and by Scilly and High (1986).

The *R–W* method was effectively that used by C.S. Robinson (1944) is his correlation of damage effects. He gives various limits of damage for the explosion of a 100 000 lb charge of high explosive. Some of these are shown in Table 17.45 together with the equivalent scaled distance $R/W^{\frac{1}{3}}$.

Table 17.45 *Some limits of the effects of the explosion (charge weight 100 000 lb) of a high explosive charge (after C.S. Robinson, 1944)*

Effect	*Limit of effect* (ft)	*Scaled distance* $R/W^{\frac{1}{3}}$ $(ft/lb^{\frac{1}{3}})$
Minor damage, inner zone	1 000	21.5
Average serious damage	1 180	25.4
Earthquake damage, normal ground	2 100	45.2
Average missile flight	5 000	108
Minor damage outer zone	10 000	215
Average glass breakage limit	100 000	2 150

Extensive work on the correlation of structural damage to buildings has been done by the Explosives Storage and Transport Committee (ESTC) in the UK. The aim of the work was the setting of safety distances for the storage of explosives. The work has been described by Jarrett (1968).

The classification of housing damage used by Jarrett is shown in Table 17.46, section B. Jarrett gives the following equation for the determination of the average circle radius for each damage category:

$$R = \frac{kW^{\frac{1}{3}}}{[1 + (7000/W)^2]^{\frac{1}{6}}} \qquad [17.32.39a]$$

where R is the average circle radius for the specified damage category (ft) and W is the mass of explosive (lb). The constant k has the values shown in Table 17.47, section A. An alternative formulation is to express the circle radius in terms of the RB value, or ratio of the radius to the radius R_B for the B damage category, and

Table 17.46 *Housing damage categories*

A Wartime damage categories (Ministry of Home Security, 1945)

A	Complete demolition
B	Partial demolition – houses not repairable and will need to be demolished
C	Houses so badly damaged as to be uninhabitable, but are repairable
D	Houses not so badly damaged as to be uninhabitable, but sufficiently so as to cause appreciable discomfort or inconvenience

Beyond D damage area, there will be considerable amount of minor damage to roof coverings, odd windows, etc.

B Jarrett damage categories (Jarrett, 1968)

A	Almost complete demolition
B	50–75% external brickwork destroyed or rendered unsafe and requiring demolition
Cb	Houses uninhabitable – partial or total collapse of roof, partial demolition of one to two external walls, severe damage to load-bearing partitions requiring replacement
Ca	Not exceeding minor structural damage, and partitions and joining wrenched from fittings
D	Remaining inhabitable after repair – some damage to ceilings and tiling, more than 10% window panes broken

C Damage categories given by Scilly and High (1986)

A	Houses completely demolished, i.e. with over 75% of the external brickwork demolished
B	Houses so badly damaged that they are beyond repair and must be demolished when opportunity arises. Property is included in this category if 50–75% of the external brickwork is destroyed, or in the case of less severe destruction the remaining walls have gaping cracks rendering them unsafe
Cb	Houses which are rendered uninhabitable by serious damage, and need repairs so extensive that they must be postponed until after the war. Examples of damage resulting in such conditions include partial or total collapse of roof structures, partial demolition of one or two external walls up to 25% of the whole, and severe damage to load-bearing partitions necessitating demolition and replacement
Ca	Houses that are rendered uninhabitable, but can be repaired reasonably quickly under war-time conditions, the damage sustained not exceeding minor structural damage, and partitions and joinery wrenched from fixings
D	Houses requiring repairs to remedy serious inconveniences, but remaining habitable. Houses in this category may have sustained damage to ceilings and tilings, battens and roof coverings, and minor fragmentation effects on walls and window glazing. Cases in which the only damage amounts to broken glass in less than 10% of the windows are not included

these ratios also are given in section A. In SI units, Equation 17.32.39a becomes

$$R = \frac{kW^{\frac{1}{3}}}{[1 + (3175/W)^2]^{\frac{1}{6}}} \qquad [17.32.39b]$$

where R is the distance (m) and W is the mass of explosive (kg). The corresponding values of k are given in Table 17.47, section B.

The average circle radii define idealized circles for which for a particular damage category the area of houses which suffer that damage outside the circle is balanced by the area of those which do not suffer such damage inside the circle. Definitions of housing damage circles are considered further in Section 17.33.

The use of the *R–W* method for the correlation of blast damage from vapour cloud explosions in the TNO correlation model has been described in Section 17.28.

17.32.8 *P–I* diagrams

The other preferred approach to the correlation of blast damage is the use of the pressure–impulse, or *P–I*, diagram.

A *P–I* diagram given by W.E. Baker *et al.* (1983) for some of the Jarrett damage categories is shown in Figure 17.93. This diagram is considered further in Section 17.33.

The use of the *P–I* diagram method is inhibited by the fact that there are few *P–I* diagrams available in the literature.

17.32.9 Window damage

The shattering of glass is an important blast damage effect, since flying glass can cause severe injury. It is considered in Section 17.40.

17.33 Explosion Damage to Housing

Explosion damage to housing is usually expressed in the form of distance-charge, or *R–W*, relations or of pressure–impulse, or *P–I*, relations. In the description just given of these two methods the application considered is housing damage.

The ESTC, or Jarrett, equation (Equation 17.32.39a) has for some decades held the field as the principal method of determining housing damage, but within the last decade several proposals have been made for the modification of this basic *R–W* correlation or its

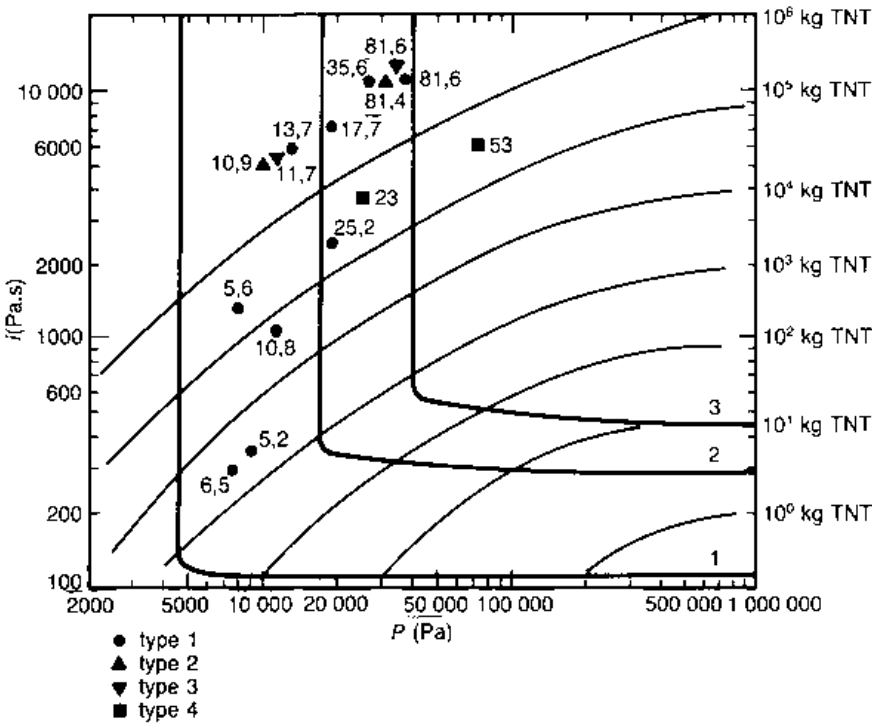


Figure 17.93 *Damage effects of explosions: P–I diagram for housing damage – 1 (after W.E. Baker et al., 1983; Mercx, Weerheijm and Verhagen, 1993). Curves are those given by the first set of authors and are as follows: curve 1, threshold for minor structural damage; curve 2, threshold for major structural damage; curve 3, threshold for partial demolition. Experimental points are those given by the second set of authors and refer to the percentage damage (expressed as building costs) for house types 1–4: type 1, two floor wooden house; type 2, two floor masonry house; type 3, single floor wooden house; type 4, two floor masonry house*

Table 17.47 *Constants and RB distances for the Jarrett equation*

A Equation constants (British units) and RB ratios (Jarrett, 1968)

Damage category	*Constant, k*	*RB ratio*
A	9.5	0.675
B	14	1
Cb	24	1.74
Ca	70	5
D	140	10

B Equation constants (SI units) and RB ratios (after Jarrett, 1968)

Damage category	*Constant, k*	*RB ratio*
A	3.8	0.675
B	5.6	1
Cb	9.6	1.74
Ca	28	5
D	56	10

C Equation constants (SI units) and RB ratios (Gilbert, Lees and Scilly, 1994c)

Damage category	*Constant, k*	*RB ratio*
A	4.8	0.675
B	7.1	1.00
Cb	12.4	1.74
Ca	21.3	3.0
D	42.6	6.0

associated *P–I* diagram, including the work of Scilly and High (1986) and Gilbert, Lees and Scilly (1994b,c).

Before considering this more recent work it is appropriate to consider the background to the Jarrett equation.

17.33.1 Housing damage categories

During the Second World War it became the practice in the UK to assign air raid housing damage to the categories A, B, Cb, Ca and D.

There are several definitions of these categories, as shown in Table 17.46. Section A of the table gives the definitions used in report S104, one of the wartime reports of the Ministry of Home Security (1945). A slightly different set of definitions is given in the paper by Jarrett (1968) describing explosives safety distances as shown in section B of the table. Section C of the table, from Scilly and High (1986), contains further amplification of the definitions.

Some wartime reports use an undifferentiated C damage category to describe Cb damage.

17.33.2 Philip equation

In an analysis of wartime damage the following equation is derived in a Ministry of Works report REN 558 by Philip (1945) for the distance R_B for B category damage. In the original British units the equation is

$$R_B = \frac{14W^{\frac{1}{3}}}{[1+(7000/W)^2]^{\frac{1}{6}}} \qquad [17.33.1a]$$

where R is the distance (ft) and W is the mass of explosive (lb). In SI units this equation is

$$R_B = \frac{5.6W^{\frac{1}{3}}}{[1+(3175/W)^2]^{\frac{1}{6}}} \qquad [17.33.1b]$$

where R is the distance (m) and W is the mass of explosive (kg). The mass of explosive is quoted as the TNT equivalent. This equation was adopted as a standard.

Gilbert, Lees and Scilly (1994c) have reviewed the basis of Equation 17.33.1a as described by Philip (1945). They conclude that although she referred to the mass of explosive in several weapons and incidents in terms of the TNT equivalent, she appears to have used in the equation a mass of explosive W which is the actual mass of explosive and to have based the equation on data for SC bombs, all of which had the same charge/weight ratio, so that strictly speaking the equation is applicable only to this family of weapons. For other weapons she gives a set of calibration constants, or correction factors.

Equation 17.33.1a was effectively endorsed in a report to the ESTC by Healy (1959), who applied it to a large number of incidents.

17.33.3 Jarrett equation

The paper by Jarrett (1968), already mentioned, was the first open publication of, and gave wider currency to, Equation 17.33.1a. He also gave explicit constants for the A, Cb, Ca and D damage categories. In British units, Jarrett's equation is

$$R = \frac{kW^{\frac{1}{3}}}{[1+(7000/W)^2]^{\frac{1}{6}}} \qquad [17.33.2a]$$

where R is the distance (ft) and W is the mass of explosive (lb). In SI units this equation is

$$R = \frac{kW^{\frac{1}{3}}}{[1+(3175/W)^2]^{\frac{1}{6}}} \qquad [17.33.2b]$$

where R is the distance (m) and W is the mass of explosive (kg). Equation 17.33.2a is frequently referred to as the Jarrett equation. The values of the constant k given in British units by Jarrett and the SI equivalents are given in Table 17.47, sections A and B, respectively. The RB ratios are also given.

Equation 17.33.2a was given by Jarrett in a paper on explosives safety distances. He states that his equation is derived from an analysis by the ESTC of 24 well documented explosions and from study of records of explosions dating from 1871 and from experience of enemy bombing in the UK. He also mentions another examination by the ESTC of 110 reports of accidental explosions. He further states that the quantity of explosive involved ranged from 300 lb to 5.3 million lb, and the types of explosive included dynamite, TNT,

Table 17.48 *Housing damage model of Gilbert, Lees and Scilly: some characteristics of the model*[a] (Gilbert, Lees and Scilly, 1994c)

Effective charge (kg)	R_B *distance* (m)	*Scaled distance* ($m/kg^{\frac{1}{3}}$)	*Peak overpressure* (Pa)	*Impulse* (Pa s)
100	10.4	2.24	2.19×10^5	606
200	16.5	2.82	1.32×10^5	609
500	30.3	3.82	0.717×10^5	614
1 000	47.6	4.76	0.473×10^5	623
2 000	72.5	5.76	0.340×10^5	650
5 000	115	6.71	0.266×10^5	759
10 000	151	6.99	0.250×10^5	917
20 000	192	7.07	0.245×10^5	1 140

[a] Revised equation for housing damage: some characteristics of damage circle equation for B damage.

Torpex and guncotton. However, Jarrett seemingly overlooked the fact that Equation 17.33.1a was derived for the specific case of SC bombs. The effect of this is that Equation 17.33.2a purports to apply to weapons in general but does not in fact allow for the effect of the weapon casing on the blast potential.

With regard to the constants quoted by Jarrett, these appear to derive from the paper by Healy. Copies of this paper contain hand-written notes suggesting values of the constants for all the damage categories (A–D). For A, B and Cb damage these values are those of Philip. The latter does not, however, give values for Ca and D damage. The values for Ca and D damage of RB = 5 and RB = 10, respectively, quoted by Jarrett, are evidently taken from the hand-written notes in Healy's paper. In the text of this paper, however, these RB values refer to window breakage rather than housing damage.

Summarizing, the Jarrett equation – Equation 17.33.2a – is in effect the Philip equation – Equation 17.33.1a – as endorsed by Healy, but with extensions to other damage categories as just described.

17.33.4 Housing damage circles

The radius used in Equation 17.33.2 is the average circle radius (ACR) for the damage category. It is defined as the radius of the circle such that the number of houses inside the circle which do not suffer the defined degree of damage is balanced by the number outside which do; this radius is denoted here as $R_{100/0}$. Use is sometimes made of another radius, R_{50}, the radius at which there is a 50% probability of a defined degree of damage. Conceptually, these two radii are quite distinct. In practice, they will often have similar numerical values. They converge where the intensity of the physical phenomenon decays rapidly and where its effect on the target passes through a narrow zone from zero to 100% effect. A quantitative treatment has been given by Lees, Poblete and Simpson (1986).

It is convenient to mention at this point another method of expressing housing damage. This is the use of the following relation to obtain from the observed values of R_A, R_B and R_C an average value $\bar{R}_B$:

$$\bar{R}_B = \frac{1}{3}\left(\frac{R_A}{0.675} + \frac{R_B}{1.0} + \frac{R_C}{1.74}\right) \qquad [17.33.3]$$

17.33.5 Model of Gilbert, Lees and Scilly

A revision of the Jarrett equation has been undertaken by Gilbert, Lees and Scilly (1994b,c), based on analysis of the original wartime documents for damage from bombs, V-1 flying bombs and V-2 rockets.

These authors first analyse the effective charge of the various weapons used, allowing for the particular explosive filling and for the effect of the casing. They then analyse the damage done by each type of weapon.

From this analysis they conclude that for B category damage the value of the constant k to be used in Equation 17.33.2b in SI units should be 7.1 instead of 5.6. They also give revised values of the constant for the other damage categories, as shown in Table 17.47, section C.

It may be noted that whereas the k values for A, B and Cb category damage are somewhat higher than those given by Jarrett, the values for Ca and D damage are less. The RB values for A, B and Cb damage are the same but those for Ca and D damage are less. These latter values agree with those proposed by Scilly and High (1986) in an earlier critique.

The model of Gilbert, Lees and Scilly is therefore Equation 17.33.2b with the constants given in Table 17.47, section C. In terms of the R_B distance this equation is

$$R_B = \frac{7.1W^{\frac{1}{3}}}{[1 + (3175/W)^2]^{\frac{1}{6}}} \qquad [17.33.4]$$

where R is the distance (m) and W is the mass of explosive (kg).

Some characteristics of the revised equation are illustrated in Table 17.48.

17.33.6 *P–I* diagrams

The housing damage correlations just given are *R–W* correlations. As described above, it is also possible to correlate housing damage in terms of a *P–I* diagram.

The *P–I* diagram for housing damage based on the Jarrett equation by given by W.E. Baker *et al.* (1983) has been given above as Figure 17.93. This diagram is reproduced in the *Green Book*.

This same diagram has been quoted by Mercx, Weerheijm and Verhagen (1991), who have plotted on it data from experimental tests detailed by Glasstone and

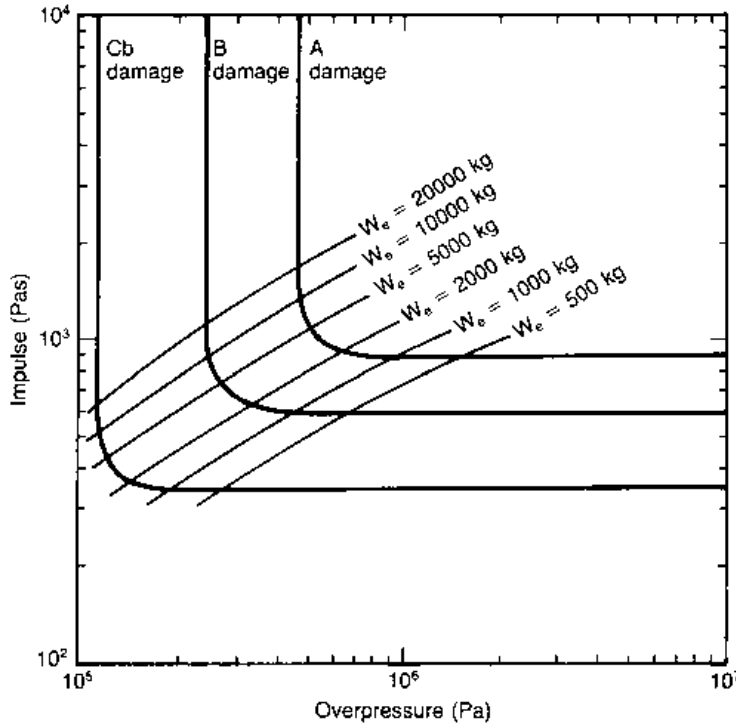


Figure 17.94 *Damage effects of explosions: pressure impulse (P–I) diagram for housing damage – 2 (Gilbert, Lees and Scilly, 1994c)*

Dolan (1980). These data also are shown in Figure 17.93. The figure shows iso-damage curves for B, Cb and Ca category damage.

The corresponding *P–I* diagram given by Gilbert, Scilly and Lees, constructed from the data in Table 17.48, is shown in Figure 17.94. The figure shows iso-damage curves for A, B and Cb category damage.

In Figure 17.94, the influence of the two variables, peak overpressure and impulse, may be examined by moving orthogonally from a curve for a category of less severe damage to that for the next most severe category. The iso-damage curves have peak overpressure and impulse asymptotes. On the right hand side of the diagram, in the region of lower charge weights, the curves exhibit impulse symptotes. In moving orthogonally from a lower damage to higher damage curve, there is an increase in impulse but not in overpressure. In other words, in this region an increase in damage occurs due to an increase in impulse. By contrast, in the top left region of the diagram, that of higher charge weights, the curves exhibit overpressure asymptotes. In moving orthogonally from a lower damage to higher damage curve, there is an increase in overpressure but not in impulse. In other words, in this region an increase in damage occurs due to an increase in overpressure. Transition occurs in the region where the charge weights are between 2000 and 5000 kg.

Thus for many charge weights of interest both peak overpressure and impulse are relevant. For this reason housing damage is correlated by Gilbert, Lees and Scilly directly in terms of charge weight rather than in terms of overpressure.

For the same reason they take the scaled distance appropriate to housing damage as

$$z' = \frac{R}{W^{\frac{1}{3}}/[1 + (3175/W)^2]^{\frac{1}{6}}} \qquad [17.33.5]$$

where z' is a modified scaled distance ($m/kg^{\frac{1}{3}}$).

17.34 Explosion Damage by Missiles

If the explosion occurs in a closed system, fragments of the containment may form missiles. In addition, objects may also be turned into missiles by the blast.

Accounts of missiles are given in *Explosions, Their Anatomy and Destructiveness* (C.S. Robinson, 1944), *Structural Defence* (Christopherson, 1946), the *Textbook of Air Armaments* (Ministry of Supply, 1952) and *Explosion Hazards and Evaluation* (W.E. Baker *et al.*, 1983) and by V.J. Clancey (1972b), Jensen (1972), W.E. Baker *et al.* (1975, 1978), Holden and Reeves (1985) and Pietersen (1985).

Much of the early work on missiles and relates to artillery and other projectiles. Basic work in the field is described by Didion (1860), by Helie (1884), by Petry (1910) and by Cranz and Becker (1921). Further work by the military on ballistics includes that of Gurney (1943, 1946). Other data derive from civil defence work such as that of Christopherson (1946).

Studies have also been made of missiles from the bursting of gas filled vessels in relation to aerospace systems and nuclear power plants. These include work by D.E. Taylor and Price (1971), Pittman (1972a,b, 1976), Bessey (1974) and Bessey and Kulesz (1976), W.E. Baker *et al.* (1975, 1978) and Garrison (1975).

An significant source of large missiles in process plant incidents is BLEVEs. Studies of the missiles from such sources have been described by Holden and Reeves (1985) and Pietersen (1985).

17.34.1 Some incidents involving missiles

The generation, size and range of missiles, and the damage which they can cause, have already been discussed to some extent above, mainly in relation to BLEVEs.

Table 17.49 gives some major incidents which involved either escalation by missiles or near misses. Some of the fragments generated in the explosion at Mexico City are shown in Plate 36.

17.34.2 Sources, types and generation of missiles

Missiles are generally classified as primary and secondary. Primary missiles are those resulting from the bursting of a containment so that energy is imparted to the fragments which become missiles. Secondary missiles occur due to the passage of a blast wave which imparts energy to objects in its path, turning them into missiles. Missiles from the bursting of a wall due to an internal explosion are treated here as primary missiles.

Accounts of the source, types and generation of primary missiles include those of Ardron, Baum and Lee (1977), J.H. Bowen (1980), Munday (1980), Porter (1980), Tulacz and Smith (1980) and W.E. Baker *et al.* (1983).

As far as concerns primary missiles from plant, three cases are commonly distinguished: case 1, bursting of a vessel into a large number of relatively small fragments; case 2, separation and rocketing of a vessel or vessel end; case 3, ejection of a single item.

17.34.3 Vessel burst pressure

The explosion energy imparted to fragments in a vessel burst is a function of the initial pressure. The various different scenarios for vessel burst pressure have been discussed in Sections 17.27 and 17.29.

17.34.4 Number and size of missiles

The number of missiles formed in an explosion involving rupture of a containment varies widely. At one extreme is the bursting of a weapon such as high explosive shell or grenade which normally gives a large number of fragments. Large numbers of missiles are also produced by fragmentation of a gas filled pressure vessel. At the other extreme is the ejection of a single item such as a valve component due to failure in a high pressure system.

Of particular interest here is rupture of a pressure vessel. This may involve either brittle or ductile fracture. The differences between these two modes of failure are discussed by Tulacz and Smith (1980). In general, failure is more likely to be ductile. Ductile failure does not usually produce missiles, but if it does they are likely to be small in number but may have potential to do severe damage. It is brittle fracture which is most likely to produce failures in which a quite large number of fragments is generated.

Failure of a vessel may occur under normal pressure loading due to a existing defect or to weakening or it may occur under abnormal pressure such as excessive gas pressure or hydrostatic pressure due to liquid expansion or explosion pressure due to combustion or reaction runaway.

In a cylindrical vessel the initiating crack is typically in the axial direction, but there is a tendency for this crack to turn and propagate circumferentially.

As already stated, for rupture of a gas filled vessel, two main modes are distinguished: (1) bursting into a large number of fragments and (2) separation into two parts. In the former case it is a common assumption that the fragments all have the same mass.

If more refined information is available, it may be correlated as a fragment mass distribution. Methods of correlation are discussed in Section 17.36.

There is some limited information available on the number of fragments formed in the bursting of pressure vessels. W.E. Baker *et al.* (1978) have compiled data on the number and size distribution of fragments for 25 accidental bursts as shown in Table 17.50. The corresponding fragment mass distributions for some of the event groups are shown in Figure 17.95.

Another such compilation is that of Scilly and Crowther (1992). This work is described in Section 17.34.21.

For BLEVEs, Schulz-Forberg, Droste and Charlett (1984) have described tests on fire engulfed vessels, one output from which is plots of the fall of fragments.

A specific study of fragments from BLEVEs has been made by Holden and Reeves (1985). For non-fire events they found that there were three events which gave one fragment, one giving two fragments, one giving three fragments, two giving four fragments and one giving seven fragments. Further information is given in Section 17.34.19.

17.34.5 Initial velocity of missiles

There are a number of different approaches to the estimation of the initial velocity of a missile. They include consideration of (1) the force or pressure on the missile, (2) the transfer of momentum to the missile and (3) the transfer of energy to the missile.

The force acting on a missile depends on the scenario. Considering first the rupture of a pressure vessel containing gas, the overpressure may occur due to a slow application of pressure or due to an explosion which gives a very high rate of pressure rise. The bursting of the vessel gives rise to a shock wave. In principle, there are two forces which act to accelerate the fragments from the vessel. One is the differential between the gas pressure and the ambient pressure. The other is the dynamic pressure, or wind. In practice, as described below, the pressure differential acts only for a very short

Table 17.49 *Some incidents involving escalation, or near misses, by missiles*

Marrietta, OH, 1962
Benzene vapours from a 6 in. relief valve on a phenol plant ignited and an explosion occurred. Flying debris ruptured pipework, releasing flammable liquids.

Louisville, KY, 1965
A compressor circulating gaseous monovinylacetylene exploded. Fragments from the explosion, together with jet flames and transmssion through piping, led to a series of further explosions.

Feyzin, France, 1966
A refinery storage sphere suffered a BLEVE, throwing pieces of steel up to 100 ton some three-quarters of a mile. One fragment cut the legs from under an adjacent sphere, toppling it and breaking its 8 in. connecting pipe. Another landed on a pipeway and severed 40 lines.

Texas City, TX, 1969
A 100 ft high refinery column disintegrated, apparently due to detonation of vinyl acetylene. Pieces were distributed uniformly over a radius of 1500 ft. One section weighing some 800 lb travelled 3000 ft.

Romeoville, IL, 1977
Roof fragments from an exploding cone roof tank in a refinery struck a covered floating roof tank and a floating roof tank, both of which ignited.

Abqaiq, Saudi Arabia, 1978
Jetting effects of gas escaping from a pipeline threw a 22 ft pipe section 400 ft, where it struck the vapour space of a storage spheroid and released further flammable vapour.

Texas City, TX, 1978
Rupture of a refinery storage sphere due to overpressure led to a large vapour cloud fire. This set off a series of BLEVEs which generated numerous missiles, causing further vessel failures. In addition to the original sphere, two further spheres, five horizontal bullets and four vertical bullets were destroyed.

Bantry Bay, Eire, 1979
Explosions on an oil tanker at the jetty generated numerous mssiles. One fragment weighing 1000 lb was found at the foot of a large crude oil storage tank 1800 ft from the ship.

Linden, NJ, 1979
A vapour cloud entered an unused control room. When the cloud exploded, debris from this building severed pipes, releasing more hydrocarbons.

Ponce, Puerto Rico, 1979
A 13 ft diameter dimerizer vessel suffered massive failure. The 15 ton steel end travelled 1900 ft and struck an adjacent paraxylene plant, setting it on fire.

Mexico City, Mexico, 1984
See Appendix 4

Romeoville, IL, 1984
A massive failure occurred of a 55 ft high $\times$ 8 ft diameter refinery absorption column. Most of the vessel was propelled 3500 ft where it struck and toppled a 138 kV power transmssion tower. Later in the incident, a piece of a vessel which had suffered a BLEVE travelled 500 ft, shearing off pipes.

Pascagoula, MS, 1986
Fragments, from an explosion in the area of a batch still, punctured two atmospheric storage tanks and a pressure storage vessel, releasing flammable material.

Grangemouth, UK, 1987
Overpressure of a low pressure separator due to gas 'breakthrough' caused the 30 ft high $\times$ 10 ft diameter vessel to disintegrate. One piece weighing 3 tons was thrown 3300 ft

Torrance, CA, 1987
A propane treater vessel failed and rocketed into a central pipe rack, cutting several pipes, including the refinery flare lines.

Antwerp, Belgium, 1989
An explosion on an ethylene oxide distillation column caused a large fire and generated missiles which did extensive damage throughout the plant.

Table 17.50 *Behaviour of fragments in some vessel explosions – 1 (W.E. Baker et al., 1978)*

Event group	*No. of events*	*Material*	*Source energy* (J)	*Vessel details*		*No. of fragments*
				Shape	*Mass* (kg)	
1	4	Propane, anhydrous ammonia	$1.49–5.95 \times 10^5$	Rail tank car	25542–83 900	14
2	9	LPG	3814–3921	Rail tank car	25 464	28
3	1	Air	5.2×10^{11}	Cylinder pipe and spheres	145 842	35
4	2	LPG, propylene	550	Semitrailer (cylinder)	6343–7840	31
5	3	Argon	$244–1133 \times 10^{10}$	Sphere	48.3–187	14
6	1	Propane	24.8	Cylinder	512	11

time, and the acceleration of the fragments is due essentially to the dynamic pressure.

Another scenario is the rupture of a partition wall by an explosion. Again the forces acting on the fragments from the wall are the pressure differential between the front face of the wall and the ambient pressure and the dynamic pressure. In principle, if the pressure incident on the wall is that of a rapidly rising blast wave and the wall configuration is such that the pressure differential across it persists until the wall ruptures, the relevant pressure is the reflected pressure. If, on the other hand, the pressure on the wall rises relatively slowly, the pressure differential is simply that between that pressure and the ambient pressure. In practice, in either case, the pressure differential again usually acts only for a very short time and the acceleration of the fragments is due mainly to the dynamic pressure.

Another approach for the bursting of a gas filled vessel is to estimate the fraction of the available energy which is converted into the kinetic energy of the fragments. This approach echoes that used is in the treatment of fragments from weapons.

For the ejection of an item such as a valve spindle by a high pressure jet of fluid, an approach based on conservation of momentum is convenient.

Some of the methods for the estimation of missile acceleration and initial velocity are now considered.

17.34.6 Initial velocity of missiles: fragmentation of a gas filled vessel

For missile acceleration and initial velocity, the first case considered (case 1) is that of the bursting of a gas filled vessel into a large number of fragments. Accounts of this include those of C.V. Moore (1967), D.E. Taylor and Price (1971). Ardron, Baum and Lee (1977), Munday (1980) and Baum (1984, 1987). Experimental work is described by Glass (1960) and Pittman (1972a,b).

An account of the initial velocity of fragments from vessels has been given by Ardron, Baum and Lee (1977). They distinguish two main fundamental treatments, one based on the stored energy and the other on fluid mechanics. The models of C.V. Moore (1967) and Munday (1980), given in Sections 17.34.7 and 17.34.8, respectively, exemplify these two approaches. Another family of methods, also based on fluid mechanics, has developed from a model of D.E. Taylor and Price (1971), who studied the rocketing of the two hemispheres from the symmetrical rupture of a sphere. This work was developed by Bessey (1974), Bessey *et al.* (1976) and W.E. Baker *et al.* (1978), who extended it, respectively to cases of spheres giving more than two equal fragments, cylinders giving multiple equal fragments and both spheres and cylinders giving multiple unequal fragments.

This work has indicated that the fraction of the energy of explosion which translates to kinetic energy of the fragments is relatively low. A more realistic model of this energy has been developed by Baum (1984), as described in Section 17.34.9.

A variant of the problem of the bursting of a gas filled vessel is the rupture of a pipe. Since the pipe is usually part of a pressure system to which it is connected, it is much less easy in this case to define the relevant available fluid energy.

17.34.7 Initial velocity of missiles: Moore model

In the stored energy, or energy partition, method the initial kinetic energy, and velocity, of the fragments is obtained from the energy stored in the vessel. This method has been used by C.V. Moore (1967). The stored energy is obtained by methods such as those given in Section 17.4. Then

$$\frac{M_v u_i^2}{2} = E_f M_f \qquad [17.34.1]$$

where E_f is the energy stored in the vessel per unit mass of fluid, M_f is the mass of fluid stored, M_v is the mass of the vessel itself and u_i is the initial velocity of the fragment. Then

$$u_i = (2E_f M_f / M_v)^{\frac{1}{2}} \qquad [17.34.2]$$

The assumption underlying Equation 17.34.1 is that all the fragments have the same velocity. Some support for this is given in the observations of Glass (1960) and Pittman (1972a) that when a vessel breaks into many pieces, fragments moving in different directions attain comparable terminal velocities.

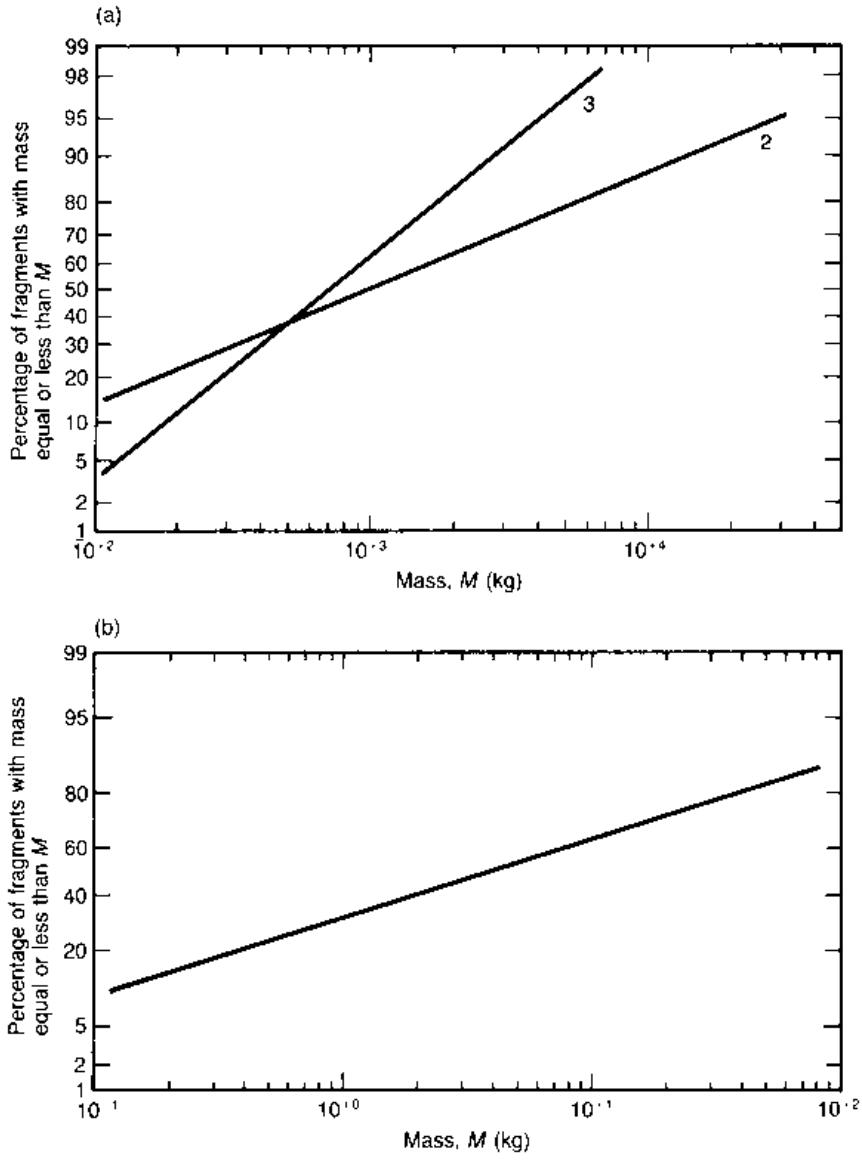


Figure 17.95 *Missile effects of explosions – fragment mass distribution from some accidental events (W.E. Baker et al., 1978): (a) event groups 2 and 3; (b) event group 6*

Moore has also given for the initial velocity of fragments from vessels semi-empirical formulae which are extensions of the well known formula of Gurney (1946) for the initial velocity of fragments from a cased explosive. His formula is

$$u_i = 1.1(E_f K)^{\frac{1}{2}} \qquad [17.34.3]$$

with

$$K = \frac{M_f}{M_v(1 + 3M_f/5M_v)} \qquad \text{Sphere} \qquad [17.34.4]$$

or

$$K = \frac{M_f}{M_v(1 + M_f/2M_v)} \qquad \text{Cylinder} \qquad [17.34.5]$$

where K is a geometric factor.

Ardron, Baum and Lee have compared the predictions of Equations 17.34.2 and 17.34.3 with experimental results for the bursting of a sphere containing superheated water. For this case, Equations 17.34.2 and 17.34.3 overestimate the measured fragment velocities by factors of 5 and 4, respectively. In other words, in this

case only about 3% of the fluid energy is imparted to the fragments.

The relations for the available energy of fluid filled vessels given in Section 17.4 yield results which show that the available energy of a gas filled vessel exceeds by an order of magnitude that of a similar liquid filled vessel. Hence the above result for the water filled vessel is not unexpected. However, Ardon, Baum and Lee also report that even for a gas filled vessel agreement between the measured velocities and the predictions of Equation 17.34.2 was only slightly better than for the water filled case. It would seem, as the authors suggest, that Equation 17.34.2 should be regarded as giving an upper bound on the initial velocity.

17.34.8 Initial velocity of missiles: Munday model

An alternative approach based on the fluid mechanics of the shock wave has been described by Munday (1980). In this model the process of acceleration is envisaged as occurring in the following way. When the vessel ruptures, there is a phase in which the fragment is accelerated by the pressure differential between the gas and the surrounding air, but the duration of this phase is very short, being related to the time for a sound wave to traverse the fragment. Thus the fragment is surrounded by moving gas before an appreciable increase in velocity has occurred.

The acceleration is caused by the dynamic pressure, or wind. The equation of motion of the fragment may be written as

$$m\frac{\mathrm{d}u}{\mathrm{d}t} = C_{\mathrm{D}}A\rho_{\mathrm{g}}(u_{\mathrm{g}} - u)^2 \qquad [17.34.6]$$

where A is the mean presented area of the fragment, C_{D} the drag coefficient, m is the mass of the fragment, u is the velocity of the fragment, u_{g} is the velocity of the surrounding gas and ρ_{g} is the density of that gas.

The velocity of the surrounding gas is related to that of the shock front. This latter velocity is determined using an empirical model. The velocity of the surrounding gas is then obtained assuming that it falls linearly from that at the shock front to zero at a distance halfway between the shock front and the centre of the vessel.

Methods are available for the characterization of the shock front in the bursting of a vessel. Brinkley and Kirkwood (1961) have given a theoretical model. Ardron, Baum and Lee (1977) have plotted the experimental results on bursting of gas filled vessels of Larsen and Olson (1957) and Pittman (1972a) to show the extent to which they fit a TNT equivalent model; the fit is fair with considerable scatter.

17.34.9 Initial velocity of missiles: explosion energy

Expressions for the energy of explosion in a vessel burst are given in Section 17.4. The two principal relations are the Brode equation (Equation 17.4.29) and the Baker equation (Equation 17.4.31).

However, it is apparent from the foregoing that only a fraction of the energy of explosion appears as kinetic energy of the fragments. This has long been appreciated. Various estimates of this fraction are available in the literature. Those given in the *High Pressure Safety Code* have been quoted in Section 17.4. Another value given by Porter (1980) is some 5–10%.

The above problem has been addressed by Baum (1984), who takes as his starting point the Baker equation (Equation 17.4.31), written in the form

$$E_{\mathrm{k}} = k\frac{P_1V_1}{\gamma_1 - 1} \qquad [17.34.7]$$

with

$$k = 1 - \left(\frac{P_{\mathrm{o}}}{P_1}\right)^{(\gamma-1)/\gamma} \qquad [17.34.8]$$

where E_{k} is the explosion energy imparted to the fragments and k is a parameter. Baum then treats k as a constant to be evaluated. From experimental data reported in the literature he found the value of k to vary between 0.2 and 0.5. On this basis the CCPS (1994/15) proposes that for rough initial calculations a value of $k = 0.2$ be used.

As stated, the foregoing applies to a vessel filled with an ideal gas. As described in Section 17.4, if this is not the case, the energy of explosion is affected. If the fluid is not an ideal gas but is instead a non-ideal gas, vapour or flashing liquid, the energy of explosion should be obtained from thermodynamic data using the method given in Section 17.4.

The CCPS refers to work by Wiederman (1986a,b) on cases involving non-ideal gases and vapour and vapour–liquid systems. In general, the effect of gas non-ideality is to reduce somewhat the initial velocity of the fragments. In some limited tests, the effect of a flashing liquid was found to cause some increase in fragment velocity compared with an ideal gas fill. For this case the CCPS quotes the fraction of the energy of explosion, estimated from thermodynamic data, which translated to kinetic energy of fragments as some 20%.

17.34.10 Initial velocity of missiles: separation and rocketing of a gas filled vessel

The second case (case 2) is that of the separation of a gas filled vessel into two parts and the rocketing of one or both of these.

The two parts which separate may be two equal halves such as the two hemispheres of a spherical vessel or two unequal ones such as the end and body of a cylindrical vessel. In either case the rapid discharge of fluid results in a strong reaction force on the separating parts of the vessel.

Models for this situation have been given by D.E. Taylor and Price (1971) and by Tulacz and Smith (1980).

The model of Tulacz and Smith (1980) is a single equation for conservation of momentum. The authors give the following illustration of the results obtained. For an autoclave of volume 0.238 m^3 and mass 3131 kg at a pressure of 41.38 bara, from which the head, with area 0.114 m^2 and mas 598 kg, blows off the initial discharge produces a rapid initial acceleration but the velocity attained is only 12 m/s.

17.34.11 Initial velocity of missiles: model of Baker *et al.*

As already mentioned, another method of estimating the initial velocity of fragments from a vessel burst has been developed by W.E. Baker *et al.* (1975, 1978), and is described by W.E. Baker *et al.* (1983). The method covers spherical and cylindrical vessels breaking into two equal fragments or into n equal fragments as shown in

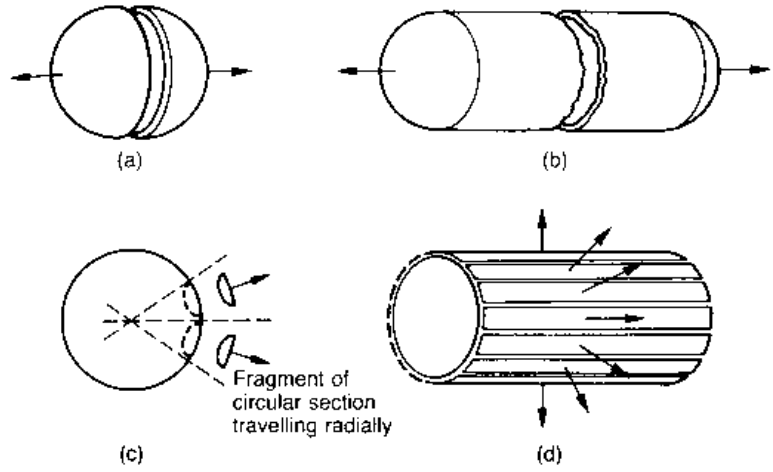


Figure 17.96 *Missile effects of explosions – generation of missiles from vessels (W.E. Baker et al., 1983): (a) sphere bursting into two equal fragments; (b) cylinder bursting into two equal fragments; (c) sphere bursting into n equal fragments; and (d) cylinder bursting into n equal strip fragments (Courtesy of Elsevier Science Publishers)*

Figure 17.96. The velocities are obtained from a parametric study based on the equations of motion of the fragments, solved using a computer code. The results are correlated in terms of a dimensionless pressure $\bar{P}$ defined as

$$\bar{P} = \frac{(p - p_o)V_o}{M_c a_g} \qquad [17.34.9]$$

and a dimensionless initial velocity $\bar{u}_i$

$$\bar{u}_i = \frac{u_i}{Ka_g} \qquad [17.34.10]$$

with

$$a_g = (\gamma R_m T)^{\frac{1}{2}} \qquad [17.34.11]$$

where a_g is the velocity of sound in the gas, M_c is the mass of the vessel, p is the pressure in the vessel, p_o is atmospheric pressure, R_m is the mass basis gas constant, T is the absolute temperature of the gas, u_i is the initial velocity of the fragment, V_o is the volume of the vessel, γ is the ratio of the gas specific heats and K is a constant.

For equal sized fragments, K is unity. The correlation obtained is shown in Figure 17.97(a).

These authors also give a method of estimating the initial velocity of a fragment from a cylindrical vessel with a length/diameter, or L/D, ratio of 10 breaking into two unequal parts. For this case the constant K is determined using Figure 17.97(b). The initial velocity is then obtained as before from Figure 17.97(a) with this value of K and taking n as 2.

The CCPS (1994/15) draws attention to some apparent discrepancies which cast doubt on the factor K.

17.34.12 Initial velocity of missiles: Baum model

Another method for the initial velocity of fragments from a vessel burst is that of Baum (1987), who gives a set of empirical correlations. He treat the following cases: (1) end cap breaking from a cylindrical vessel, (2) cylindrical vessel breaking into two parts in a plane perpendicular to its axis, (3) disintegration of a spherical or cylindrical vessel into multiple fragments and (4) a single small fragment ejected from a vessel. The first three of these are considered here, and the last in the next section.

The relations given by Baum utilize a parameter F which is defined as

$$F = \frac{(P_1 - P_o)r}{ma_o^2} \qquad \text{Large No. of fragments} \qquad [17.34.12]$$

$$F = \frac{(P_1 - P_o)Ar}{m_f a_o^2} \qquad \text{Small No. of fragments} \qquad [17.34.13]$$

where a_o is the speed of sound, A is the area of the detached portion of the vessel wall, m is the mass per unit area of the vessel wall, m_f is the mass of the fragment, P_o is atmospheric pressure, P_1 is the absolute initial pressure in the vessel and r is the radius of the vessel.

The correlations for the three cases referred to are then

$$u_i = 2a_o F^{0.5} \qquad \text{Cylinder end-cap} \qquad [17.34.14]$$

$$u_i = 2.18a_o[F(L/r)^{\frac{1}{2}}]^{\frac{2}{3}} \qquad \text{Two cylinder sections} \qquad [17.34.15]$$

$$u_i = 0.88a_o F^{0.55} \qquad \text{Sphere or cylinder, multiple fragments} \qquad [17.34.16]$$

where L is the length of the cylinder. In Equation 17.34.15 F is obtained using $A = \pi r^2$.

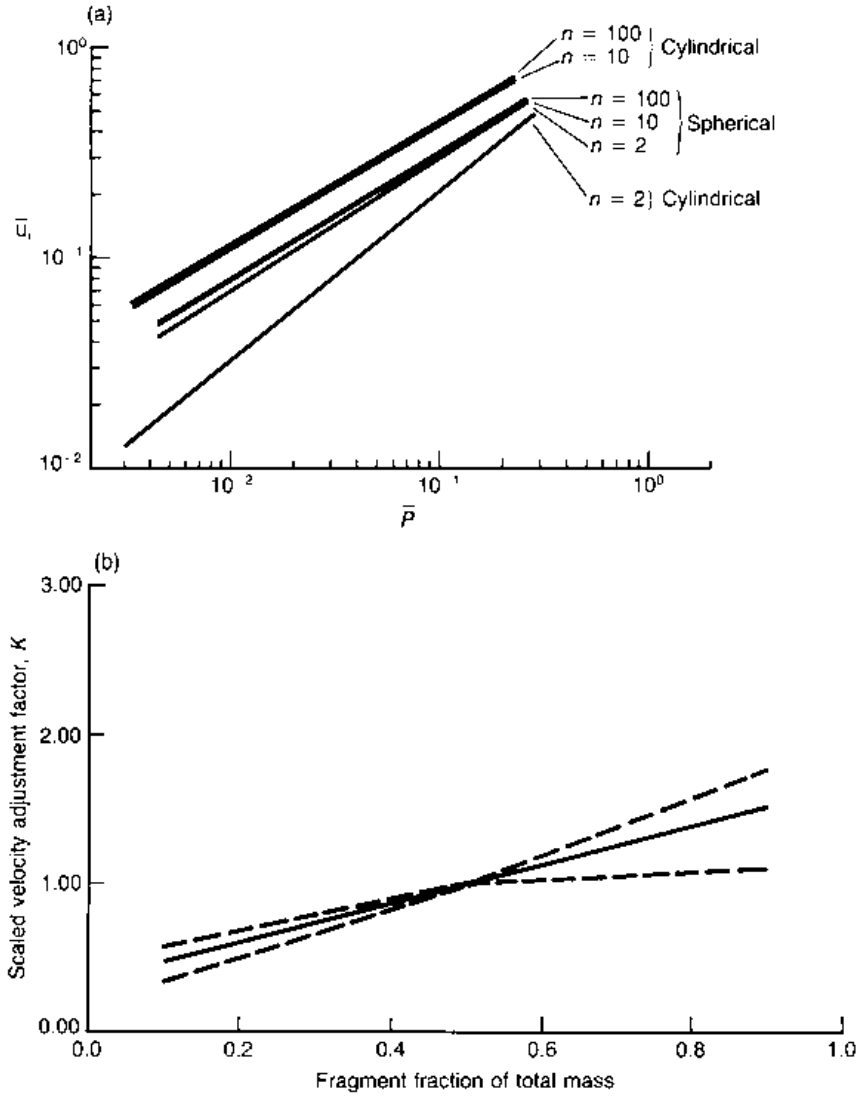


Figure 17.97 *Missile effects of explosions – initial velocity of fragments from a bursting vessel (W.E. Baker et al., 1983): (a) initial velocity correlation; (b) velocity adjustment factor for unequal masses (Courtesy of Elsevier Science Publishers)*

17.34.13 Initial velocity of missiles: ejection of a plant fitting

The third case considered here (case 3) is the ejection of a fitting such as a valve stem by a high pressure jet of gas. This is a relatively well defined situation, and modelling based on fluid mechanics is appropriate. Models have been developed by a number of workers, including Cottrell and Savolainen (1965), Gwaltney (1968) and Ardron, Baum and Lee (1977).

The usual approach is based on momentum transfer. The momentum of the jet is assumed to be transferred to the missile and the residual momentum of the jet is neglected.

Gwaltney (1968) has given a number of simple analytical methods for particular cases of ejection of fittings by a jet of gas.

Ejection of a small fragment from a cylindrical vessel is one of the cases treated by Baum as described in the previous section. For this case he gives

$$u_i = 2a_o\left(\frac{Fs}{r}\right)^{0.38} \qquad s < 0.3r;\ \gamma = 1.4;\ 20 < P_1/P_o < 300 \qquad [17.34.17]$$

where s is the dimension of the fragment.

17.34.14 Initial velocity of missiles: comparison of methods

The comparison of methods made by Ardron, Baum and Lee (1977) has already been mentioned. Another more recent comparative study is that of Baum (1984). This is discussed and extended by the CCPS (1994/15).

The following are some of the findings of the CCPS comparative study.

In comparing models, use is made of the scaled energy, which is defined as

$$\bar{E} = \left(\frac{2E_{ex}}{Ma_o^2}\right)^{\frac{1}{2}} \qquad [17.34.18]$$

where $\bar{E}$ is the scaled energy, E_{ex} is the energy released in the explosion and M is the mass of the vessel.

An upper limit to the initial velocity of the fragments is set by the case of a hypothetical massless fragment for which the velocity is the maximum velocity of the expanding gas, or peak contact surface velocity. This velocity is a function of the pressure ratio P_1/P_o.

Differences between models tend to become significant for small values of the scaled energy.

The Moore model, which is based on high explosion energies, whilst tending to give an upper limit value, nevertheless compares quite favourably with other models for both low and high energies.

In the lower energy range the CCPS discusses the relative merits of the models of Baum and Baker *et al.* For certain specific comparisons Baum's model yielded higher velocities for spheres but lower ones for cylinders.

17.34.15 Angle of departure of missiles

In order to determine the flight of a missile it is necessary also to have information on the angle of departure. The extent to which this is known depends on the particular case. For ejection of a fitting, the direction of the gas jet and, hence, the angle of departure of the fitting is usually defined. Likewise, this will generally be so for the two parts in the separation and rocketing of a gas filled vessel.

The angles of departure in the case of the bursting of a gas filled vessel into a large number of fragments is less well defined. The common assumption is that the fragments are projected uniformly in all directions. Alternatively, the more conservative approach may be adopted in which the spatial density of the fragment is assumed to be greater in the direction of the vulnerable targets.

For some methods the results for an individual fragment can be sensitive to the angle of departure. The CCPS (1994/15) report this to be the case for the model of rocketing fragments.

17.34.16 Shape and air resistance of missiles

The behaviour of the fragment in flight depends on its shape. Some fragments are chunky, with dimensions similar along the three main axes, while others are less symmetrical, with dissimilar lengths along these axes.

A fragment in flight is acted on by a lift force normal to the trajectory and a drag force along the trajectory. These forces are defined in Equations 17.34.47 and 17.34.48 below in terms of a drag coefficient C_D and a lift coefficient C_L.

In ballistic terms a fragment may be characterized as a drag-type fragment if it is chunky so that for any orientation $C_D \gg C_L$ and as a lifting type fragment if it is such that for some orientation $C_L \geq C_D$.

The force resisting the flight of the missile is a function of its velocity, but the relationship is not a simple one. The velocity range of interest for projectiles is termed the ballistic range. At very low velocities, below the ballistic range, the resistance is proportional to the velocity. At ballistic but subsonic velocities the resistance is proportional to the square of the velocity. At supersonic velocities the resistance is a complex function.

17.34.17 Flight of missiles

The flight of a projectile is a standard problem in mechanics and is treated in texts on this topic (e.g. Synge and Griffiths, 1960; R.C. Smith and Smith, 1968; B. Brown, 1969).

Three cases are considered here: case 1, no air resistance, case 2, air resistance proportional to the velocity, and case 3, air resistance proportional to the square of the velocity. The first case is not realistic and results in gross overestimates of velocity and range, but provides a useful illustration of the general approach. The third case is realistic for ballistic velocities in the subsonic range.

Considering first the flight of a projectile in the absence of air resistance (case 1), the equations of motion are

$$\frac{d^2x}{dt^2} = 0 \qquad [17.34.19]$$

$$\frac{d^2y}{dt^2} + g = 0 \qquad [17.34.20]$$

where g is the acceleration due to gravity, t is time, and x and y are the distances in the horizontal and vertical directions, respectively.

Since there is no horizontal component of acceleration, in the x direction, both at $t = 0$ and subsequently

$$\frac{dx}{dt} = u_i \cos\alpha \qquad [17.34.21]$$

where u is the velocity along the line of flight, α is the angle of departure and the subscript i denotes initial. Integrating with initial conditions $t = 0$, $x = 0$

$$x = u_i(\cos\alpha)t \qquad [17.34.22]$$

In the y direction, at $t = 0$

$$\frac{dy}{dt} = u_i \sin\alpha \qquad [17.34.23]$$

Integrating Equation 17.34.20 with initial conditions $t = 0$, $dy/dt = u_i \sin\alpha$

$$\frac{dy}{dt} = u_i(\sin\alpha) - gt \qquad [17.34.24]$$

Integrating again with initial conditions $t = 0$, $y = 0$

$$y = u_i(\sin\alpha)t - \frac{1}{2}gt^2 \qquad [17.34.25]$$

For t from Equation 17.34.22

$$t = \frac{x}{u_i \cos \alpha} \quad [17.34.26]$$

For the relation between x and y, eliminating t from Equations 17.34.22 and 17.34.25

$$y = x \tan \alpha - \frac{gx^2}{u_i^2 \cos^2 \alpha} \quad [17.34.27]$$

For the distance travelled, or range, setting $y = 0$ in Equation 17.34.27

$$x = \frac{u_i^2 \sin^2 \alpha}{g} \quad [17.34.28]$$

For the velocity u

$$u = \left[\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2\right]^{\frac{1}{2}} \quad [17.34.29]$$

Then from Equations 17.34.21, 17.34.24 and 17.34.29

$$u = [u_i^2 - 2u_i(\sin \alpha)gt + g^2t^2]^{\frac{1}{2}} \quad [17.34.30]$$

For the angle of approach to earth, or angle of return, β noting that

$$\tan \beta = \frac{dy}{dx} = \frac{dy}{dt}\frac{dt}{dx} \quad [17.34.31]$$

from Equations 17.34.21 and 17.34.24

$$\tan \beta = \tan \alpha - \frac{gt}{u_i \cos \alpha} \quad [17.34.32]$$

For the return to earth, the maximum range, which occurs at a projection angle of 45°, is

$$x = \frac{u_i^2}{g} \quad [17.34.33]$$

For the time of return to earth from Equation 17.34.25 with $y = 0$

$$t = \frac{2u_i \sin \alpha}{g} \quad [17.34.34]$$

For the angle of approach β at the point of return to earth, or angle of return, from Equations 17.34.32 and 17.34.34 $\tan \beta = -\tan \alpha$. For the velocity at return to earth from Equations 17.34.30 and 17.34.34 $u = u_i$.

For a projectile subject to a resistance k proportional to the velocity (case 2), the equations of motion are

$$\frac{d^2x}{dt^2} + k\frac{dx}{dr} = 0 \quad [17.34.35]$$

$$\frac{d^2y}{dt^2} + k\frac{dy}{dt} + g = 0 \quad [17.34.36]$$

Following an approach similar to that for the first model, it can be shown that

$$\frac{dx}{dt} = u_i \cos \alpha \exp(-kt) \quad [17.34.37]$$

$$\frac{dy}{dt} = \frac{1}{k}(ku_i \sin \alpha + g)\exp(-kt) - \frac{g}{k} \quad [17.34.38]$$

$$x = \frac{u_i \cos \alpha}{k}[1 - \exp(-kt)] \quad [17.34.39]$$

$$y = \left(\frac{u_i}{k} \sin \alpha + \frac{g}{k}\right)[1 - \exp(-kt)] - \frac{gt}{k} \quad [17.34.40]$$

For a projectile subject to a resistance proportional to the square of the velocity (case 3), the equations of motion are

$$\frac{d^2x}{dt^2} + k\left(\frac{dx}{dt}\right)^2 = 0 \quad [17.34.41]$$

$$\frac{d^2y}{dt^2} + k\left(\frac{dy}{dt}\right)^2 + g = 0 \quad [17.34.42]$$

Beyond this point, the attempt to apply to cases 2 and 3 the treatment used for case 1 becomes increasingly intractable.

However, there is an alternative approach which for case 3 yields much simpler results. This involves working in terms not of the velocity u along the flight path but of the velocity v relative to the ground. The relation between the two initial velocities is

$$v_i = u_i \cos \alpha \quad [17.34.43]$$

The relevant equation of motion is

$$\frac{dv}{dx} + kv = 0 \quad [17.34.44]$$

which is obtained from Equation 17.34.41 utilizing $dt/dx = 1/v$. Integrating with initial conditions $x = 0$, $v = v_i$

$$v = v_i \exp(-kx) \quad [17.34.45]$$

An empirical formula which allows for air drag quoted by V.J. Clancey (1972b) is

$$v = v_i \exp(-kax/w^{\frac{1}{3}}) \quad [17.34.46]$$

with

$k = 0.002$ Velocity supersonic

$= 0.0014$ Velocity subsonic

where a is the drag coefficient, v is the velocity of the projectile (ft/s), v_i is the initial velocity of the projectile (ft/s), w is the mass of the projectile (oz), x is the distance travelled by the projectile (ft) and k is a constant. The drag coefficient a is a function of fragment shape but is generally approximately 1.5–2.

Equation 17.34.46 is of the same form as Equation 17.34.45. It also appears to be related to the equations for the flight of fragments from exploding weapons given by Christopherson and quoted in Section 17.36.

17.34.18 Range of missiles

The range of a missile in the absence of air drag is given by Equation 17.34.28 and the maximum value of that range for an angle of departure of 45° by Equation 17.34.33.

However, these relations greatly overstate the actual ranges obtained. For example, using the initial velocities from TNT charges given by V.J. Clancey (1972b) as quoted in Section 17.36, ranges of 5×10^5 ft and upwards are obtained. Therefore, it is clearly necessary to take air drag into account.

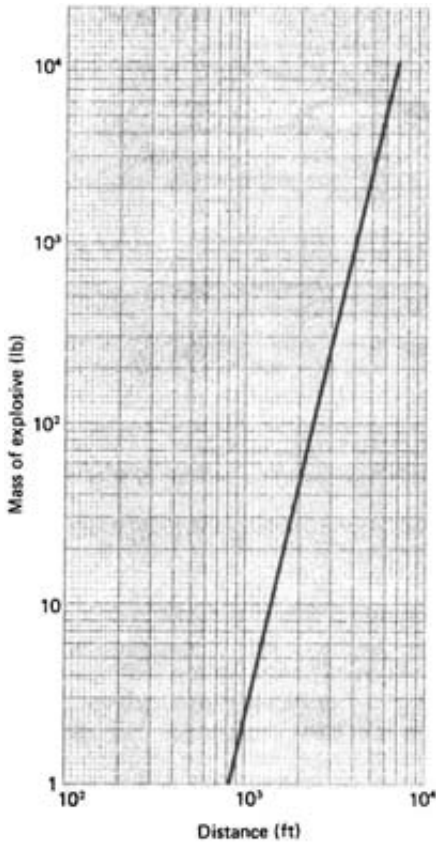


Figure 17.98 *Missile effects of explosions: maximum horizontal range of fragments from a cased charge of TNT on the ground surface (V.J. Clancey, 1972b)*

Clancey also gives a relation for the maximum horizontal range of fragments from a cased charge of TNT on the ground surface as shown in Figure 17.98. The correlation is based on experimental determination with TNT in lightweight containers. Most of the fragments do not travel the maximum distance, but fall at distances between 0.3 and 0.8 of the maximum.

The probability that there would be at least one fragment which travels the maximum distance increases with the number of fragments and is therefore greater for a large explosion.

As stated above, a fragment in flight is acted on by a lift force, which is normal to the trajectory and opposes gravity, and a drag force, which is along the trajectory. These forces are

$$F_L = C_L A_L \frac{\rho u^2}{2} \qquad [17.34.47]$$

$$F_D = C_D A_D \frac{\rho u^2}{2} \qquad [17.34.48]$$

where A_D is the drag area, A_L is the lift area, C_D is the drag coefficient, C_L is the lift coefficient, F_D is the drag force, F_L is the lift force, u is the velocity of the fragment and ρ is the density of the air.

A fundamental approach to the estimation of fragment range has been developed by W.E. Baker *et al.* (1975, 1978) and is described by W.E. Baker *et al.* (1983). The range is obtained by solving the equations of motion for acceleration of the fragment in the horizontal and vertical directions, utilizing for the drag and lift forces Equations 17.34.47 and 17.34.48. The results are correlated in terms of the dimensionless velocity $\bar{u}_i$, defined as

$$\bar{u}_i = \frac{C_D A_D \rho_o u_o^2}{Mg} \qquad [17.34.49]$$

and the dimensionless range $\bar{R}$

$$\bar{R} = \frac{C_D A_D \rho_o R}{M} \qquad [17.34.50]$$

and the lift/drag ratio

$$= \frac{C_L A_L}{C_D A_D} \qquad [17.34.51]$$

where g is the acceleration due to gravity, M is the mass of the fragment, R is its range, u_o is its initial velocity and ρ_o is the density of air. The treatment is based on the assumption that the fragment is spinning and applies to fragment velocities up to Mach 1 or about 340 m/s. The equations were solved using the computer code FRISB.

The correlation obtained is shown in Figure 17.99. For values of the lift/drag ratio not given, interpolation can be used, but becomes inaccurate on the steep portions of the curve.

Many fragments from explosions are chunky and have a lift coefficient C_L, and hence lift/drag ratio, of zero. Other fragments may be pieces of plate for which the lift/drag ratio is more complex. A method of estimating the lift/drag ratio for these latter is given in their Appendix E by W.E. Baker *et al.* (1983).

Data on missile flight are available in many descriptions of accidental explosions. Jacobs *et al.* (1973) state that in the explosion at the American Oil Company refinery at Whiting, Indiana (Case History A22):

> The vessel fragments were scattered for several hundred feet away from the unit site. One 60–ton piece landed on a tank of gasoline, smashing it severely and igniting and scattering its contents.

The investigation of the explosion at the Dow Chemical Company's works at King's Lynn by the HSE (1977b) gives a map of the fragments from the explosion (Case History A81). In one ship explosion investigated by V.J. Clancey (1976b) a deck cover of 400 ton was thrown 100 ft.

The study of accidental explosions by W.E. Baker *et al.* (1978) referred to in Section 17.34.4 and tabulated in Table 17.50 also yielded data on fragment range. The graphs of fragment range for the different event groups are shown in Figure 17.100.

17.34.19 Missiles from BLEVEs

A particular type of explosion which is prone to generate missiles is the BLEVE. A study of missiles from BLEVEs has been described by Holden and Reeves (1985).

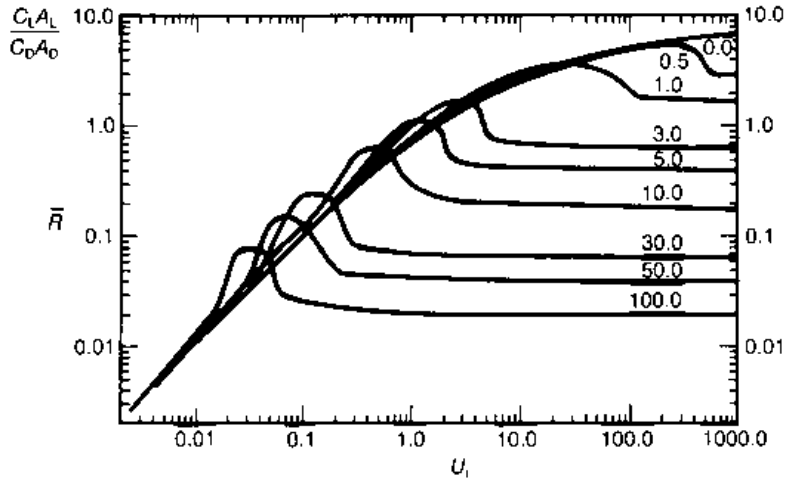


Figure 17.99 *Missile effects of explosions: distance travelled by missiles (W.E. Baker et al., 1983) (Courtesy of Elsevier Science Publishers)*

Much of the information obtained in the work relates to vessels used in transport, but no reason was seen why it should not apply to fixed plant also. A distinction is made between cylindrical and spherical vessels, which are treated separately. For cylindrical vessels information was obtained on (1) probability of fragment generation, (2) number of fragments, (3) range of fragments and (4) direction of fragments, and for spherical vessels on the last three features.

For cylindrical vessels there were 113 events involving fire on which sufficient information was available and of these 89 involved fragment generation. The probability of fragment generation was estimated from this as 0.8.

The number of fragments generated by a cylindrical vessel was obtained for 27 events involving LPG vessels and ranged from one to four. The number of events generating one, two, three and four fragments were 8, 7, 10 and 4, respectively. This excluded a fire engulfment test at White Sands reported by C. Anderson and Norris (1974), in which 10 fragments were generated and which appears to be anomalous in comparison with the accident data.

The range of fragments was taken as the ultimate end point after landing and travelling across the ground, through structures, etc. The range for fragments from LPG vessels is shown in Figure 17.101. Figure 17.101(a) gives the range for all events together with a comparison with data from an earlier study by W.E. Baker *et al.* (1978). Figure 17.101(b) shows the effect of vessel size and Figure 17.101(c) the difference between end tub fragments and other fragments. There is a clear tendency for fragments from vessels with a capacity $<90\,m^3$ and for end tubs to travel further. Figure 17.101(d) gives the range for fragments from spherical vessels. A further graph is given for the range of fragments from vessels containing ammonia, ethylene oxide and vinyl chloride.

The authors comment that the ranges found tend to be much less than those obtained from theoretical estimates of maximum range using the corresponding launch angle, which can exceed 3 km to first ground impact, that launch angle is important, and that their empirical data include implicit allowance for factors such as launch angle, inventory, etc.

With regard to direction of fragments from cylindrical vessels, for some 11 incidents involving 15 vessels, mainly LPG, about half the fragments were projected into about a third of the total area, in arcs of 30° to either side of the vessel front and rear axial directions. The correlation given for LPG vessel fragments is shown in Figure 17.102.

For spherical vessels the sample of events was only seven. The number of fragments generated in these vents was 3, 4, 5, 5, 6, 16 and 19, giving an average of 8.3 fragments per event. This number is appreciably higher than for cylindrical vessels.

Figure 17.101(d) shows that the range of the fragments from spherical vessels is marginally higher than for cylindrical vessels.

Fragments from spherical vessels tend to be projected in a non-uniform distribution of directions. Taking the favoured direction in each incident and treating this as an arbitrary 0° and then overlaying the plots for the individual incidents to give an overall plot divided into 30° sectors, it was found that a fragment is 17 times more likely to be projected in the favoured direction than in the least favoured.

The authors describe a number of incidents where fragments from BLEVEs have caused damage or injury. At Crescent City a propane rail tank car exploded, generating two main fragments, one of which punctured the head of another such tank and the other sheared the housing and valves off a third tank (Case History A50).

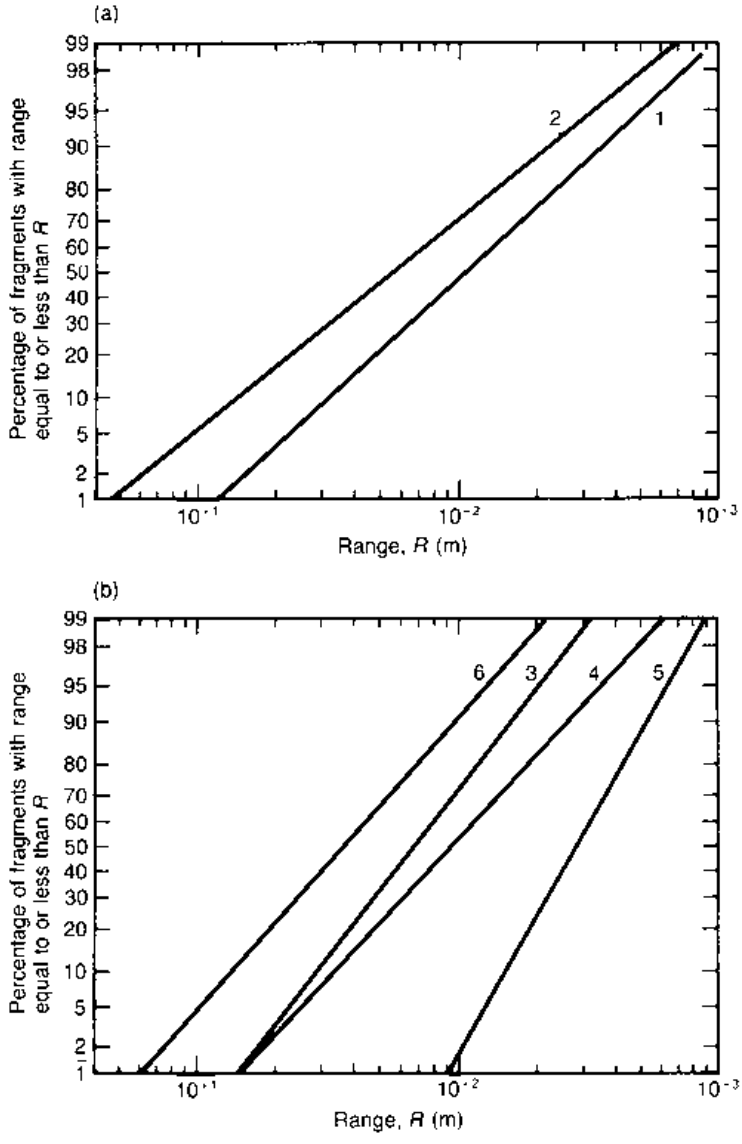


Figure 17.100 *Missile effects of explosions: fragment range distribution from some accidental events (W.E. Baker et al., 1978): (a) event groups 1 and 2; (b) event groups 3–6*

Similarly, at Laurel a fragment from the BLEVE of a tank car pierced another propane tank car (Case History A44).

Escalation may also occur by disablement of other equipment. At Laurel a fragment from one of the rail tank cars hit a pumphouse and cut an 8 in. water main, reducing the fire water pressure. At Puebla, Mexico, in 1977 a fragment from the BLEVE of a vinyl chloride storage sphere hit the main site water tank and carried it across the perimeter fence (Case History A87). At Texas City in 1978 a fragment from the BLEVE of an LPG sphere travelled 210 m and hit the site fire water tank.

Fragments from BLEVEs are also a cause of injury. In the LPG road tanker BLEVE at Deer Lake, Pennsylvania, in 1959 it was a rocketing fragment which was responsible for most of the 11 dead and 10 injured. These bystanders were at a distance of more than 200 m and beyond the range of thermal hazard in that case. At West St Paul, Minnesota, in 1974 fragments from the BLEVE of an LPG storage vessel were held responsible for the deaths of three fire fighters and a bystander.

A further study of missiles from BLEVEs is that of Pietersen (1985), who investigated the disaster at Mexico

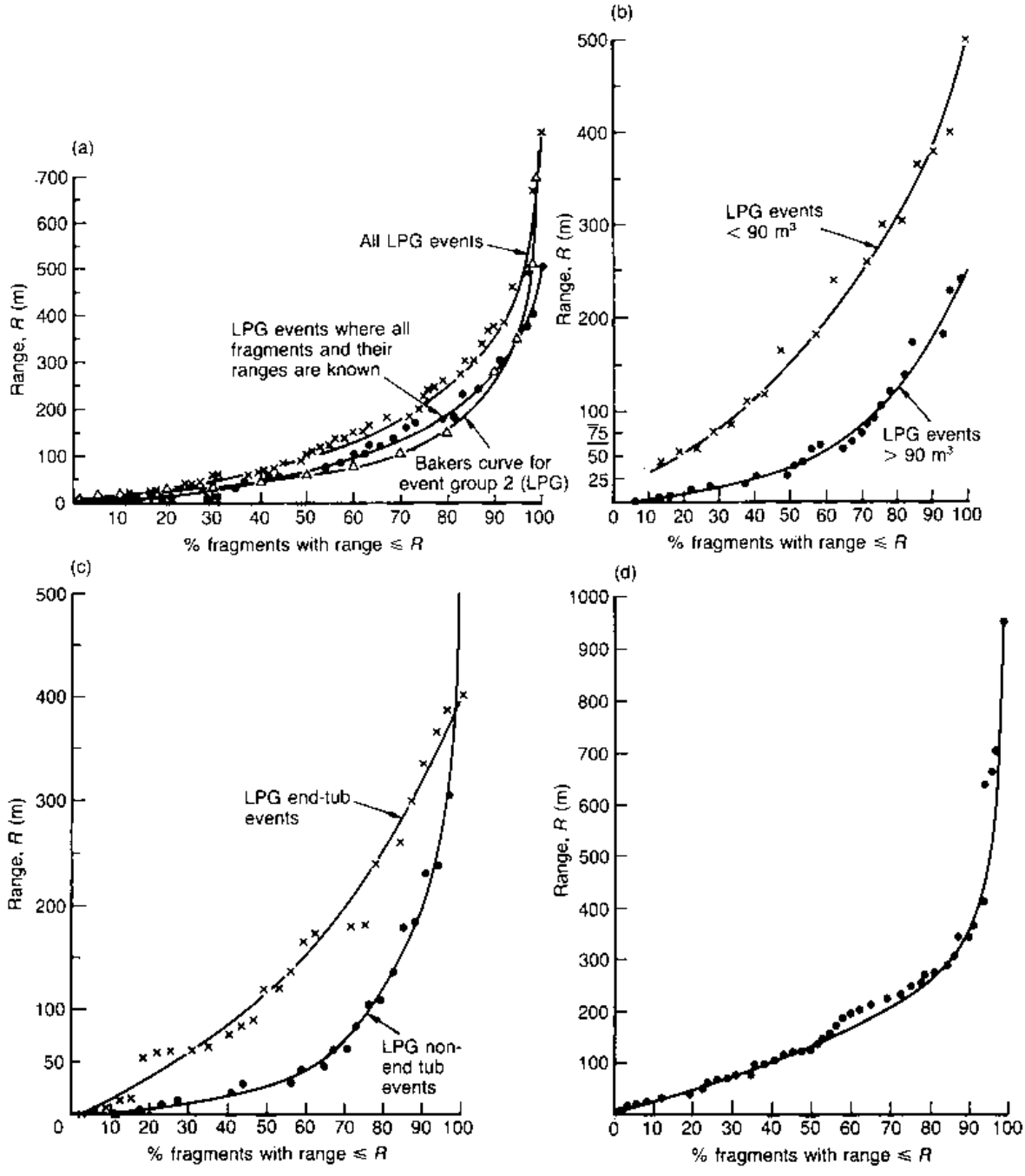


Figure 17.101 *Missile effects of explosions: distance travelled by missiles from bursting of LPG vessels (Holden and Reeves, 1985): (a) all events; (b) effect of vessel size; (c) end tub and other fragments; (d) spherical vessels (BLEVEs) (Courtesy of the Institution of Chemical Engineers)*

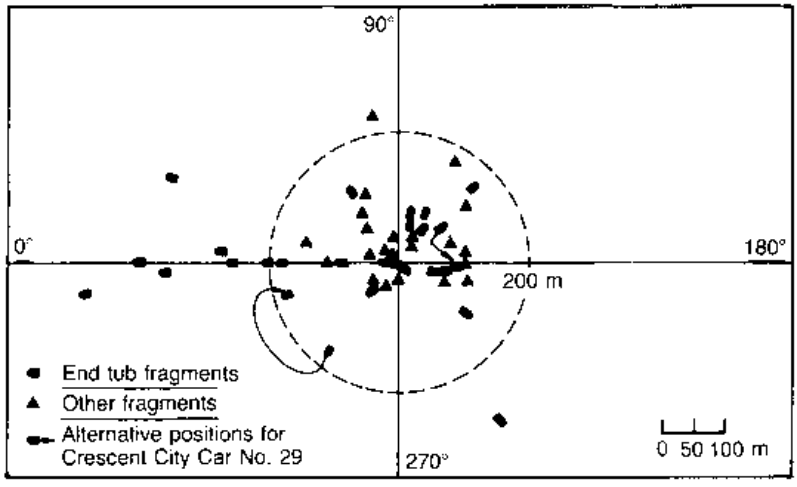


Figure 17.102 *Missile effects of explosions: direction of travel of missiles bursting of LPG vessels (Holden and Reeves, 1985) (Courtesy of the Institution of Chemical Engineers)*

City, Mexico, in 1984, described in Appendix 4. For 44 cylindrical bullet tanks he found that 4 were still on their supports and a further 11 still in their original bund, and that of the remaining 29, the distribution of bullets and end tubs was as follows:

Distance (m)	*No. of fragments from bullets*	*No. of fragments from end tubs*
<100	17	3
100–200	4	4
200–300	3	3
300–400	2	2
400–700	1	1
700–1000	1	1
1000–1200	1	1
Total	29	15

For the spheres, 25 major fragments were collected lying as follows: 6 within 100 m, 6 between 100 and 200 m, 7 between 200 and 300 m, 1 between 300 and 400 m, 3 between 400 and 500 m, one between 500 and 590 m and one at 590 m.

Pietersen discusses the mechanism of rocketing of part of a cylindrical bullet. He takes as the energy transferred to the missiles 60% of the total available energy of a gas filled vessel as given by the Brode equation and then utilizes a relation equivalent to Equation 17.34.1. On this basis he obtains for the larger vessels on the site

Vessel volume (m^3)	*Vessel mass* (kg)	*Initial velocity of missile* (m/s)
270	70	149
1600	215	206
2400	300	214

which gives maximum velocities of about 150 m/s for cylinders and 200 m/s for spheres. He also quotes a velocity of 60 m/s for the vapour of the LPG in the cylinder undergoing flash vaporization. He states that calculations based on these figures indicate that without lift the maximum range of the fragment is of the order of 360 m, though the figure is not very accurate. It is sufficient to show, however, that lift must play a significant role.

17.34.20 CCPS method

The CCPS *Fire and Explosion Model Guidelines* (1994/15) include as part of the treatment for BLEVEs a method for fragments.

The method used for the estimation of the energy of explosion used has been described in Section 17.27.

For the number of fragments the value of the scaled energy given by Equation 17.34.18 is used to discriminate between the case where the fragments are few and that where they are numerous. The region where the scaled energy lies between 0.1 and 0.4 is one where the number of fragments generated tends to be small.

Use is also made of Baker's event groups as described in Section 17.34.4. An event group is selected which approximates the case in hand, and the event group data are then used to obtain an estimate of the expected number of fragments and of their mass distribution.

For the initial velocity of the fragments three methods are given. Method 1 is to obtain the energy of explosion using the methods given in Section 17.34.9 and to apply to it a factor of 0.2 to obtain the kinetic energy available to the fragments and then to assume this is distributed equally among the fragments as in Equation 17.34.1. Method 2 is that of Baker *et al.* outlined in Section 17.34.11. Method 3 is that of Moore, which is given here as Equation 17.34.3. The choice of method to use is governed by the scaled energy relation 17.34.18.

For the range distribution of the fragments use is made of the method of Baker *et al.*, which is described in Section 17.34.18.

Ranges may also be estimated using the event group data.

17.34.21 Missile damage method of Scilly and Crowther

A method for assessment of the risk of missile impact on a process plant site has been described by Scilly and Crowther (1992).

These authors give data on the fragments generated in eight incidents, as shown in Table 17.51.

The method which they describe involves for a given target estimation of the following features: (1) the number of fragments, (2) the range distribution, (3) the mass distribution, (4) the orientation factor, (5) the effective range interval and (6) the probability of a strike.

They illustrate the method by reference to the case of a distillation column 50 m high, 2.4 m diameter and 12.5 mm thick subject to a sudden pressure increase due to a rapid decomposition.

In general, the number N of fragments depends on a variety of factors, including the vessel size and shape, the material of construction, the operating temperature and the rate of pressure rise. The authors obtain the estimate of the number N of fragments by inspection of Table 17.51. For their illustrative example they take N as 35.

As already described, the distribution of fragments may exhibit directionality. The authors suggest there is some justification for allowing for this by the use of a correction factor of 2, applied to N.

For the distribution of the ranges of the fragments, they utilize not the fragment with maximum range R_{max} but that with the next farthest range, or penultimate range, R_{pen}, arguing that the latter is more meaningful. The range distribution is found to be log-normal, and is fitted by the authors using a probit equation. They give the following tentative relations:

$$R_{med} = 2.8P_v \qquad [17.34.52]$$

$$R_{pen} = 4.1R_{med} \qquad [17.34.53]$$

where P_v is the vessel pressure (barg), R_{med} is the median range (m) and R_{pen} is the range of the penultimate fragment (m). A probit equation for the probability P of a fragment falling at a range R may then be constructed from the pair of points ($P = 0.5$, R_{med}) and ($P = N_{pen}/N$, R_{pen}), where $N_{pen} = N - 1$.

Given that for vessels of size exceeding 20 m^3 the great majority of fragments will have energy sufficient to penetrate steel containments, which are unlikely to have a wall thickness greater than 15 mm, the distribution of mass is much less important. However, for the case where it is desired to estimate the mass distribution for vessels of such size, the authors propose that the median mass of the fragments be taken as that of the vessel divided by 73 and that the slope of the associated probit equation be taken as 1.5.

The orientation factor F_{or} is

$$F_{or} \approx \frac{W}{2\pi R} \qquad [17.34.54]$$

where R is the range of the fragment (m) and W is the combined width of the target and the fragment (m). The width of a fragment is taken in the illustrative example as 4 m.

The target is vulnerable to any fragment falling between a minimum range R and a maximum range $R + L$, where L may be termed the effective range interval. For a target consisting of a sphere supported on legs the authors derive by geometry for fragments directed respectively at the midpoint and at the edge of the sphere

$$L = (H - r + r\sec\theta)\tan\theta + r \qquad \text{Sphere midpoint} \qquad [17.34.55]$$

$$= (H - r)\tan\theta + r \qquad \text{Sphere edge} \qquad [17.34.56]$$

where H is the height of the top of the sphere (m), L is the effective range interval (m), r is the radius of the sphere (m) and θ is the angle of descent (°). For the angle of descent the authors suggest 45° as a conservative value. They use 60° in their illustrative example.

The probability P_{ri} that a fragment falls within the effective range interval L is then determined from the probit equation for the range distribution by taking the difference between the probabilities of a fragment reaching $R + L$ and of one reaching R.

The probability of a strike P_{st} is then

$$P_{st} = F_{or}NP_{ri} \qquad [17.34.57]$$

As already stated, the authors effectively take as unity the probability of puncture of the target given a strike.

For an explosion in the vessel used to illustrate the method, described above, and for a target consisting of a sphere 12 m diameter supported on 3 m legs at 150 m distance from the exploding vessel, the authors obtain a calculated burst pressure $P_v = 45$ barg, a number of fragments $N = 35$, a range of fall between 150 and 199 m, the range probit $Y = -1.44 + 3.066\log_{10}R$, a probability that a fragment falls within the effective range interval of 0.14, an orientation factor $F_{or} = 0.016$, and a probability of strike $P_{st} = 0.08$.

17.34.22 Flying glass

Glass fragments from the breaking of windows are significant for injury of personnel. This effect is considered in Section 17.40.

17.34.23 Falling masonry and glass

Another form of missile which is relevant particularly to an explosion in a built-up area is falling masonry and glass.

A model for this hazard is included in the set of submodels in the model for a condensed phase explosion in a built-up area given by Gilbert, Lees and Scilly (1994h). A person in the street near to a building is vulnerable to falling masonry and glass. The extent of the hazard from these two sources will vary. The relative importance of falling glass may be expected to rise where the buildings in question are large city skyscrapers.

Casualties occurred from falling masonry in air raids, but the interpretation of such data needs to take account of the fact that in many cases the weapons exploded inside buildings.

The model tentatively proposed by Gilbert, Lees and Scilly (1994h) for the estimation of the risk from falling masonry and glass is as follows. The approach used is to designate a band of specified width on the pavement beside the building and to assume that persons in this

Table 17.51 *Behaviour of fragments in some vessel explosions – 2 (after Scilly and Crowther, 1992) (Courtesy of the American Institute of Chemical Engineers)*

Incident[a]	*Vessel details*			*Vessel pressure*		*No. of fragments*	*Missile range*			*Missile mass*		
	Diameter (m)	*Volume* (m^3)	*Thickness* (mm)	*Operating* (barg)	*Burst* (barg)		*Median*	*Penultimate/ median* (m)	*Probit slope*	*Median*	*Vessel/ median* (kg)	*Probit slope*
1a	3.1	90		16	75–85	29	94	4.4	1.60			
1b	7.2	1560	63	16	75–85	14	95	3.7	1.03	16 900	27	1.95
2	1.7	210	38	9	155	3						
3	2.7	57	13	0	63	10	156	3.4	1.87	170	52	1.92
4	2.3	200/53[b]	16	3	60	$\geq$50						
5	3.0	73	19	8	50	21	117	4.8	1.20	173	100	1.10
6	2.5	162	12, 16, 19	3	32[c]	35	140	4.0	2.46	539	67	1.63
7	0.94	1.3	6.5	−1	34	24	14	11.4	3.60	4	77	1.21

[a] Incidents are as follows: 1a and 1b, separator and reactor, respectively, at Whiting, Indiana, 1957 – fuel/air combustion probably leading to detonation; 2, Ponca City, 1959 – probable fuel/air combustion; Doe Run, 1962 – probable liquid phase polymerization and gas phase decomposition of ethylene oxide; Texas City, 1969 – liquid phase decomposition of vinyl acetylene; Grangemouth, 1987 – breakthrough of high pressure (155 bar) gas; Antwerp, 1987 – decomposition of ethylene oxide during distillation; Wendstone Chemicals, 1988 – liquid phase decomposition of *o*-nitrobenzaldehyde containing nitrate esters.

[b] Distillation column had volume of 200 m^3, but only the central section of volume 53 m^3 disintegrated.

[c] Authors suggest that this value is underestimated and that it should be at least 43 barg.

band do not survive. The width of the band is intended to allow both for the density and size distribution of falling debris within a wider band and for the probability of a fatality given a hit. The default value used for the width of the band is 1 m. This value is for use where the height of the building does not exceed 15 m.

17.34.24 Crater ejecta

Some explosions create a crater and in this case fragments are ejected. Craters have been treated in Section 17.31. The account here is confined to the crater ejecta.

A treatment of the fragments from cratering has been given by Richmond and Fletcher (1971). These authors base their work on data given by Henny and Carlson (1968) for crater ejecta from explosions in rock and in soil. The charges were half buried in the ground. The missiles considered are those with a mass exceeding 0.5 lb.

For the maximum range of fragments Richmond and Fletcher give the following equations:

$$R_{\max} = 70W^{0.4} \qquad \text{Rock} \qquad [17.34.58a]$$

$$= 30W^{0.4} \qquad \text{Soil} \qquad [17.34.58b]$$

where R is the range (ft) and W is the mass of explosive (lb) (of TNT equivalent) and the subscript max denotes maximum.

The probability P of being struck by one or more such missiles is

$$P = 1 - \exp(-a/A) \qquad [17.34.59]$$

where a is the projected area of the body (ft^2) and A is the specific area, or surface hemispherical area per missile (ft^2/missile). The projected area a is taken as 6.2 ft^2.

The authors deal primarily with fragments from cratering in rock and consider particularly the conditions for 50 and 1% probability of being struck. The fragment specific areas at these levels of probability are 9 and 600 ft^2/fragment, respectively.

For cratering of rock the authors give a graph showing curves for the 50 and 1% probability of being hit as a function of mass of explosive and distance, but give no guidance on obtaining other values. However, their data may be correlated approximately by the following relations:

$$A = \frac{A_h}{n_e} \qquad [17.34.60]$$

with

$$n_e = \phi_n nm \qquad [17.34.61]$$

$$\phi_n = 1 \qquad R < 200 \qquad [17.34.62]$$

$$\phi_n = 3.46 - 0.466 \ln R \qquad 200 \le R \le 900 \qquad [17.34.63]$$

where A_h is the area of the hemisphere on the surface of which the human target is standing (ft^2), m is the mass of explosive (ton), n is the near field number of missiles per ton of explosive (missiles/t), n_e is the number of missiles at distance R (missiles/t), R is the distance (ft) and ϕ_n is a correction factor which allows for the reduction in the number of missiles with distance. The value of n is 230 missiles/t.

The authors state that the average mass of the missiles is well above 0.5 lb and argue that the probability of serious injury given a hit is likely to be high.

The application of this work to the cratering caused by an explosive load in a street has been discussed by Gilbert, Lees and Scilly (1994h). From an analysis of the crater in the Peterborough explosion (HSE, 1990c), which involved an explosive load equivalent to some 800 kg of TNT on a vehicle in a built-up area, they conclude that it is probably not necessary to make any correction for the height of the load above ground or for the nature of the ground, but suggest that some correction seems appropriate for the fact that in the experimental work described the charges were half buried and suggest a reduction in the near-field number n of fragments from 230 to 150 missiles/t.

17.34.25 Impact effects

There are available a number of empirical equations for estimating the penetration of fragments in various types of target. However, it is pointed out by W.G. High (1980) that most of these relations are for fragments from high energy density sources, where the sources of interest in process plant, such as high pressure vessels, are of relatively low energy density.

It is convenient to quote first some of the empirical equations for determining fragment penetration given in the *High Pressure Safety Code* by B.G. Cox and Saville (1975)*, which may be regarded as a coherent set selected by the authors for plant design purposes. Other individual formulae for penetration into reinforced concrete and into steel plate are given in Sections 17.34.26 and 17.34.27.

A treatment of the impact of missiles on pipework is given in Section 17.35.

The equations quoted in the *High Pressure Safety Code* assume penetration normal to the surface. They are valid for projectile velocities not exceeding 1000 m/s, above which there is often a quite different mechanism in which target and projectile are melted by the impact energy.

For penetration by small fragments, the depth of penetration is given by the relation

$$t = Km^{n_1}V^{n_2} \qquad [17.34.64]$$

where m is the mass of the fragment (kg), t is the thickness of the barricade needed just to stop the fragment (m), V is the velocity of the fragment (m/s), K is a constant and n_1, n_2 are indices. The values of the constant K and the indices n_1 and n_2 for different target materials are:

	K	n_1	n_2
Concrete (crushing strength 35 MN/m^2)	18×10^{-6}	0.4	1.5
Brickwork	23×10^{-6}	0.4	1.5
Mild steel	6×10^{-5}	0.33	1.0

* Reproduced with permission of the High Pressure Technology Association.

Equation 17.34.64 is valid for compact blunt steel fragments such as solid cylinders with the length equal to the diameter with a mass of not more than 1 kg.

For penetration by larger fragments the depth of penetration may be calculated from

$$t = \frac{Cm}{A} \log_{10}(1 + 5 \times 10^{-5} V^2) \qquad [17.34.65]$$

where A is the presented area of the fragment (m^2) and C is a constant. The constant C has the following values:

	C
Concrete (unreinforced, crushing strength 15 MN/m^2)	10×10^{-4}
Concrete (1.4% reinforcement, crushing strength 40 MN/m^2)	3.5×10^{-4}
Brickwork	25×10^{-4}
Mild steel	0.5×10^{-4}
Alloy steel	0.3×10^{-4}

Equation 17.34.65 applies for large blunt fragments with a mass exceeding 1 kg.

For penetration by rod shaped missiles for concrete

$$t = 2 \times 10^{-7} \frac{mV^{1.5}}{d^{1.8}} \qquad [17.34.66]$$

and for mild steel plate

$$t = \left(0.33 \times 10^{-9} \frac{mV^2}{d^3}\right)^{1/1.41} \qquad [17.34.67]$$

where d is the diameter of the fragment (m).

Fragments of irregular shape, such as are usually produced by the bursting of a pressure vessel, have much lower penetrating power, often only half, than compact blunt fragments, while pointed projectiles have appreciably more.

Further relations for impact of fragments on various types of target have been given by W.E. Baker *et al.* (1983). They consider the following targets: (1) thin metal plates and sheets, (2) roofing materials and (3) reinforced concrete. For the latter the treatment includes steel pipe, utility pole and rod missiles.

The impact relations given by these authors are correlated in terms of a non-dimensional projectile velocity, a non-dimensional target deflection and non-dimensional target thickness.

As the size of the projectile increases, the response of the target becomes more significant. Work by R.P. Kennedy (1976) has shown that the target response may be modelled by assuming it to be subject to a rectangular pulse forcing function. With this assumption it is then possible to apply conventional structural response techniques.

Another aspect of fragment impact on concrete targets is spalling and scabbing, and correlations are available for the threshold and for depth attained.

17.34.26 Impact effects: penetration of reinforced concrete

There has been a considerable amount of work on the penetration of reinforced concrete by missiles. Accounts are given by Chelapati, Kennedy and Wall (1972), R.P. Kennedy (1976), Barr *et al.* (1980), Porter (1980) and Tulacz and Smith (1980).

Some principal correlations are those of Petry (1910), the Army Corps of Engineers (ACE), the Ballistics Research Laboratory (BRL) and the National Defense Research Committee (NDRC) (1946). These correlations are given by Tulacz and Smith (1980).

Of these models, the modified NDRC correlation (NDRC, 1946) particularly appears to have found widespread acceptance. It is applicable to a flat-faced cylindrical missile. The equation is given in SI units by Barr *et al.* (1980) as follows:

$$G(x/d) = 2.74 \times 10^{-5} (Dd^{0.2}/\sigma_c^{0.5}) V^{1.8} \qquad [17.34.68]$$

with

$$G(x/d) = (x/2d)^2 \qquad x/d \leq 2 \qquad [17.34.69]$$

$$G(x/d) = (x/d) - 1 \qquad x/d > 2 \qquad [17.34.70]$$

$$D = m/d^3 \qquad [17.34.71]$$

where d is the diameter of the missile (m), D is its calibre density (kg/m^3), m is its mass (kg), V is its velocity (m/s), x is the penetration depth (m) and σ_c is the compressive strength of concrete (Pa). The limits of applicability of Equation 17.34.68 are discussed by Gwaltney (1968) and Tulacz and Smith (1980).

Equation 17.34.68 is a penetration correlation. NDRC has also developed perforation formulae for use in conjunction with this equation. These are

$$\frac{e}{d} = 3.19\frac{x}{d} - 0.718\left(\frac{x}{d}\right)^2 \qquad \frac{e}{d} < 3 \qquad [17.34.72]$$

$$\frac{e}{d} = 1.32 + 1.24\frac{x}{d} \qquad 3 \leq \frac{e}{d} \leq 18 \qquad [17.34.73]$$

where e is the perforation thickness (m). This is the thickness of target which the missile will just perforate.

Another model for penetration by a flat-nosed cylinder, again based on extensive testing, is the Commissariat à l'Energie Atomique/Electricité de France (CEA/EDF) formula, described by Berriaud *et al.* (1978) and discussed by Barr *et al.* (1980):

$$V_p^2 = 1.7\sigma_c \rho^{\frac{1}{3}} \left(\frac{de^2}{m}\right)^{\frac{4}{3}} \qquad [17.34.74]$$

where V_p is the perforation velocity (m/s) and ρ is the density of the concrete (kg/m^3); the other symbols are as defined above.

The limits of applicability of Equation 17.34.74 are discussed by Berriaud and Barr *et al.*

A three-dimensional computer code, CRASH, for the investigation of impact effects on various types of target, including reinforced concrete and steel plate, has been described by Hopkirk, Lympany and Marti (1980).

17.34.27 Impact effects: penetration of steel plate

There has also been a good deal of work on the penetration by missiles of steel plate. Accounts are given by Neilson (1980) and Tulacz and Smith (1980).

Some principal correlations are those of Christopherson (1946), Stanford Research Institute

(SRI), the Ballistics Research Laboratory (BRL) and the NDRC.

Of these models, that of SRI, described by R.W. White and Botsford (1963), appears to have found wide acceptance. It is given in SI units by Neilson as

$$\frac{e_c}{d} = \frac{u}{10.29}(42.7h^2 + wh) \qquad [17.34.75]$$

where d is the diameter of the missile (m), e_c is its critical impact energy (J), h is the thickness of the target panel (m), u is the ultimate tensile strength of the panel (Pa) and w is the width of the panel (m).

Equation 17.34.75 was derived originally for relatively long missiles striking thin panels (<7 mm thick). The limits of applicability and behaviour of the equation are discussed by Neilson and by Tulacz and Smith.

The latter also give the BRL and NDRC formulae and discuss the comparative behaviour of the three models.

Mention has already been made of the general impact computer code CRASH, which can be used for steel plates. Neilson also describes the use for this purpose of the codes EURDYN and CADROS.

17.34.28 Impact effects: impact on a storage sphere

A treatment of the impact of a fragment from a BLEVE on a storage sphere has been given by Pietersen (1985). The method involves calculating (1) the force at the point of impact to deform the sphere up to the yield point, and the corresponding energy E_y, and (2) the energy E_r to deform the sphere in the plastic region between yield and rupture. Utilizing relations given by Roark and Young (1975) and taking the impact area as five times the vessel wall thickness, these two energies are found to be $E_y = 7$ kJ and $E_r = 64$ kJ. Assuming that plastic deformation of the impacting fragment uses up an amount of energy equal to that used in the sphere itself the total energy required for rupture is 135 kJ. From simple kinetic energy considerations, for a fragment of mass 20 te (1/10th of a sphere) the velocity required to effect rupture is then 3.7 m/s and for one of 2 te (1/100th of a sphere) it is 11.6 m/s. This calculation indicates that the velocities to cause rupture are well below the initial velocities of fragments from a sphere undergoing BLEVE, which have been discussed above, and therefore that rupture of a sphere close by is to be expected.

17.34.29 Barricade design

In some cases use is made of barricades around a potential source of explosion. Barricades are utilized particularly in work with explosives, but may also be used around other potential explosion sources such high pressure equipment. There is also considerable interest in barricades in the nuclear industry.

Accounts of the design of barricades include those given in the *High Pressure Safety Code* by B.G. Cox and Saville (1975) and by Loving (1957), W.G. High (1967) and C.V. Moore (1967).

The essential first step in design of a barricade is to determine the failures against which protection is required. In other words, it is necessary to start with hazard identification.

In barricade design, provision of protection against an explosion of flammable gas is generally treated as a special case. Excluding this, the design resolves into provision of a barricade which offers resistance to (1) blast and (2) fragments. Broadly, design against blast is often based on an equivalent static pressure approach and design against fragments on fragment penetration correlations.

Design methods for barricades to protect against vessel rupture are discussed in the *High Pressure Safety Code*. It is relatively easy to provide a barricade for vessels with energy contents in the range 10^3–10^5 J, but it becomes progressively more difficult as the energy content rises, and for energy contents capable of giving a shock wave of 50×10^6 to 100×10^6 J it is usually impractical.

The preferred method is a closed cubicle. For protection against blast using the equivalent static pressure method the *Code* gives the relevant pressure as

$$P = 7.6[(E \times 10^{-6})/V]^{0.72} \qquad P < 70 \qquad [17.34.76]$$

where E is the shock wave energy (J), P is the equivalent static pressure (bar) and V is the volume of the enclosure (m^3). Equation 17.34.76 is applicable where the ratio of the maximum to the minimum dimension of the enclosure does not exceed two.

Cylindrical cubicles can be designed as thin-walled pressure vessels. Small cubicles can be made of angle iron and steel plate. Large cubicles should be of reinforced concrete. Since the shock wave has positive and negative phases, reinforcement is required on both inner and outer faces.

Some transmission of the shock wave occurs through the walls of the cubicle. This creates the hazard that persons outside may be injured by eardrum rupture. The *Code* gives the following method of estimating this. The impulse incident on an isolated wall is given as

$$I = 0.008E^{\frac{1}{3}}(R/E^{\frac{1}{3}})^{-\frac{1}{2}} \quad 0.004 < (R/E^{\frac{1}{3}}) < 0.2 \qquad [17.34.77]$$

where I is the impulse per unit area ($N\,s/m^2$) and R is the distance (m). Also for an isolated wall the initial velocity of the wall, assumed unconstrained, is

$$V = I/m \qquad [17.34.78]$$

where m is the mass of the wall per unit area and V is the velocity (m/s). For the wall of a cubicle the impulse is taken as three times the value given by Equation 17.34.77 and the initial velocity of the wall is then that given by Equation 17.34.78.

If the value of the initial velocity V so calculated is less than 10 m/s, the shock wave generated outside should be too small to cause eardrum rupture.

If the plant in the cubicle contains flammables or toxics an opening may be necessary to allow dispersion of small leaks by ventilation. The *Code* states that the design of a vented cubicle is essentially the same as that for a closed cubicle.

With a vented cubicle, however, the escaping shock wave will tend to cause overpressure similar to that which would exist if there was no cubicle and the explosion was in the open. The *Code* gives the following equation for the estimation of the peak incident overpressure:

$$P = 8.45 \times 10^{-5}(E^{\frac{1}{3}}R)^{2.3} - 0.16(R/E^{\frac{1}{3}}) + 0.06 \quad 0.004 < (R/E^{\frac{1}{3}}) < 0.2 \qquad [17.34.79]$$

where P is the peak incident overpressure (bar).

The cubicle should also withstand the fragments generated. Since the distances are usually short, such a fragment will tend to be at its initial velocity. Much of the work on fragment penetration, described above, has been done to assist with barricade design.

Safety walls may be used instead of a cubicle. For a safety wall the impulse from the blast wave is as given by Equation 17.34.77 and the initial velocity as given by Equation 17.34.78, without application of the factor of three. There will, however, be diffraction of the shock wave around the wall which is difficult to estimate.

The thickness of the barricade should be such as to enable it to withstand both shock wave and fragment penetration.

The barricade may be required to survive the simultaneous assault of the shock wave and of fragments. This problem is discussed in the *Code* and also by Moore.

Information on viewing ports for cubicles is given by Moore (1967).

17.34.30 Plant design

The hazard from missiles has not generally been a major factor in plant design, but rather more attention is now paid to it.

Design of plant for the hazard of missiles may focus on the source or on the target. On the whole it makes more sense to concentrate on the source, since the probability that a given plant item will be the target of a missile, even if a missile-generating explosion occurs, is very low.

Attention should be paid in design to features such as doors, vents and other fixtures on plant which may become missiles and measures should be taken to minimize this.

Where a serious missile hazard exists, use may be made of barricades and safety walls as described above.

17.35 Explosion Damage to Plant by Missiles

The treatment just given of missile impact effects constitutes a rather general account, with emphasis on penetration of concrete walls and steel plates. This is now supplemented by consideration of a particular problem, taken as representative for missile impacts on plant, that of damage to pipework.

The account given draws particularly on evidence given to the Piper Alpha Inquiry by A.C. Palmer (1989), which considered the mechanisms of, and potential for, damage to a 4 in. high-pressure gas condensate line in B Module from fragments from the firewall between B and C Modules set in motion by an explosion in C Module.

17.35.1 Fragment velocity and energy

The velocity and energy of fragments has been considered in the previous section. Essentially, a fragment is accelerated by a force which will vary with the circumstances. The point which is relevant here is that in a large proportion of cases, the principal force causing acceleration is that due to the dynamic pressure, or wind. The acceleration of the fragment up to its maximum velocity then requires a finite distance, which may be several metres. This fact can be significant if the target is close to the source of the fragments.

17.35.2 Distribution of energy

Only a part of the kinetic energy of the fragment is transferred to the target and is available to cause damage. Some of the energy goes into the deformation, and possible disintegration, of the fragment itself. The distribution of energy between the fragment and the target depends on their relative stiffness and is highly variable. If the fragment is more readily deformed than the target, it absorbs more energy than it transmits.

The relative stiffness is itself a function of the velocity of impact. If the impact velocity is low, the relative stiffness is governed by the overall deformation of the two objects, whilst if it is high deformation may be localized and the energy distribution may alter.

The energy transferred to the target is itself divided into that energy which causes local damage and that which causes the whole target to respond. This latter energy is taken into account in some treatments but not in others.

17.35.3 Impact effects

Before considering damage caused by the fragment, it is appropriate to mention several effects associated with the impact of a high velocity object on a steel target.

Accounts of impact and its effects include *Impact* by Goldsmith (1960) and *Impact Strength of Materials* by W. Johnson (1972).

The impact effects of principal interest here are those which bear on the effective force exerted, the effective strength of the material and the nature of the target response.

The force exerted by a rapidly applied load is twice that of a slowly applied load. Thus consider, as an approximate treatment, a vertical rod with a disc at the bottom and with an annular weight around the rod of the same radius as the disc and of mass m. Let this weight be suddenly applied from effectively zero height, to the disc so that it produces in the rod an extension x. Then by energy balance the force F exerted on the disc is

$$mgx = \frac{1}{2}Fx$$

Hence

$$F = 2mg$$

This is twice the force exerted by a static load for which $F = mg$.

If a load is applied very rapidly to a steel object so that the strain rate is high, there is an increase in the effective strength of the material. This may be expressed as the ratio of the yield stress to the static yield stress, the ratio increasing with the strain rate. From the work of N. Jones (1983) this dynamic strength factor is of the order of 2 at a strain rate of 10^2 and 3 at one of 10^3.

The nature of the impact also affects the response of the target and the mode of deformation. If the load is applied slowly, quasi-static failure modes apply, whilst if it is applied very rapidly, dynamic failure modes come into play. Further, if the velocity of impact is very high, the effect may be intense, but localized.

The rapidity of loading at which these different effects come into play varies with the effect.

Table 17.52 *Estimated minimum energy or velocity requirements for failure of the 4 in. condensate line on Piper Alpha (after A.C. Palmer, 1989)*

Mode of deformation	*Estimated minimum values*	
	Energy (kJ)	*Velocity* (m/s)
Loads applied relatively slowly		
1. Tensile failure	112	
2. Bending failure[a]	82	
3. Shear failure[b]	9	
4. Cutting		
(a) Cutting to leak[c]	11	
(b) Cutting off	143	
5. Denting		
(a) Denting by a concentrated force	36	
(b) Denting by an edge:		
Dent $\frac{1}{2}$ diameter deep	26	
Dent 1 diameter deep	70	
Loads applied very rapidly		
6. Dynamic tensile failure	19	60
7. Dynamic puncturing	7	40

[a] Bending through a 90° angle.
[b] Unlikely to occur without bending.
[c] Pipe severed over $\frac{1}{8}$ of circumference.

17.35.4 Modes of damage

Some modes of damage to pipework are exemplified by those considered in relation to the 4 in. condensate line mentioned. This pipe passed through the firewall from C Module into B Module, took a 90° bend and ran parallel to the wall, then took another 90° bend and ran away from the wall, into the main oil line. The pipe was understood to have had an outside diameter of 114 mm and a wall thickness of 11.1 mm (revised from an initial value of 8.6 mm) and to have been operating at a pressure of about 62 bar. In the analysis the steel was treated as having a yield stress of 260 N/mm^2, an elastic modulus of 210 N/mm^2, a Poisson ratio of 0.3 and a density of 7850 kg/m^3.

The modes of damage considered by Palmer are listed in Table 17.52.

17.35.5 Models for damage

In general, the energy absorbed, or work done, during deformation caused by a slowly applied load is obtained from the relation

$$U = \frac{1}{2}F\delta \qquad [17.35.1]$$

with

$$\delta = le \qquad [17.35.2]$$

where e is the strain, F is the force applied (N), l is the length of pipe stretched (m), U is the energy absorbed (J) and δ is the resultant elongation (m). As shown above, for a load applied rapidly, as in impact, the force is twice the static force.

Considering first the failure modes for a load applied relatively slowly, the tensile failure mode involves failure of a section of the pipe under tension due to application of a load which causes the ultimate tensile stress to be exceeded. For this mode, the model for energy absorbed, or work done, is given by Equation 17.35.1 using the impact force value.

For bending, two regimes were considered: elastic bending and plastic bending. When a pipe is bent, it first responds elastically and then starts to yield. Once yielding has begun, an increasing proportion of the cross-section deforms plastically, in compression on one side of the pipe and in tension on the other. The pipe cross-section becomes oval and then a buckle forms on the compression side. For this mode, the model for energy absorbed, which is that applicable to the plastic regime, the energy absorption in the elastic regime being negligible, is essentially

$$U = \phi\theta \qquad [17.35.3]$$

where θ is the angle of the bend (rad) and ϕ is the plastic moment (N m).

For shear, the limiting shear force depends on the details of the loading. One approach is to assume that the distribution of the shear stress is similar to that in a circular tube acting as a beam. An estimate may then be made of the energy for the shear displacement of one pipe wall thickness.

For cutting, two distinct modes are considered: cutting to leak and cutting off. The first involves cutting through to the extent that a leak occurs and the second cutting to the extent of a complete guillotine break. For this mode, the model used for energy absorbed is that of Lu (1989). This model is based on measurement of the

energy absorbed when a sharp rigid wedge is pushed through a flat steel plate. This energy is

$$\frac{U}{\sigma_y t^3} = 3\frac{L}{t} \qquad \frac{L}{t}\text{small} \qquad [17.35.4]$$

$$= 2.5\left(\frac{L}{t}\right)^{1.3} \qquad 5 < \frac{L}{t} < 100 \qquad [17.35.5]$$

where L is the length of the cut (m), t is the thickness (m) and σ_y is the yield stress (N/m^2). The length of the cut is taken for cutting to leak as part of the circumference and for cutting off as the whole circumference.

For denting, again two modes are considered: denting by a concentrated force and denting by an edge. These evidently correspond to denting by a blunt and by a sharp-edged object, respectively. For the first mode, in which the load is assumed to be a radial force applied over a circular area of the pipe, the model for energy absorption used is that of A.J. Morris and Calladine (1971). The force for plastic collapse is determined and the energy absorbed is obtained from this force and the depth of the dent, using Equation 17.35.1.

For the second mode of denting, in which the load is assumed to be applied by a sharp-edged object at right angles to the pipe, the model for energy absorption used is that of Wierzbicki and Myung Sung Su (1986).

Moving on to the failure modes for a load applied very rapidly, these modes occur only if at impact the fragment has a certain minimum velocity as well as the requisite minimum energy. For these modes, therefore, Table 17.52 gives minimum values for both velocity and energy.

Dynamic tensile failure is caused by the very sudden application of a tensile load. For the minimum velocity, the model used is based on the work of Kolsky (1963) on tensile plastic waves in a bar whose end is suddenly given a velocity v. It applies to the case where the velocity thus imparted exceeds that at which the steel just becomes plastic. The velocity v is related to the strain e_p behind the plastic wave front set up by the impact. If the velocity is high enough for this strain to reach the ultimate tensile strain, failure occurs. The relation between the velocity v and the strain e_p is

$$v = \int_0^{e_p} [\sigma_t(e)/\rho]^{\frac{1}{2}}\, de \qquad [17.35.6]$$

where e is the strain, e_p is the strain behind the plastic wave front, v the imparted velocity (m/s), ρ is the density of steel (kg/m^3) and σ_t is the tensile stress (N/m^2).

For the minimum energy for dynamic tensile failure, the approach is similar to that for quasi-static tensile failure described above, except that a factor, taken as 3, is applied to the yield stress to allow for the suddenness of the application of the load, or dynamic effect.

Dynamic puncturing is gouging caused by high velocity impact. For the minimum velocity the model used is based on the velocity required to raise the local compressive stress to the yield point and thus just to enter the plastic regime and is

$$\sigma_c = \rho c v \qquad [17.35.7]$$

where c is the velocity of elastic compression waves in steel (m/s), v is the velocity of impact of the missile (m/s) and σ_c is the compressive stress caused by the impact (N/m^2).

For the minimum energy for dynamic puncturing, the model used is that of W. Johnson (1972). This model gives the energy required to gouge out a cavity and is

$$U = 3\sigma_y V_c \qquad [17.35.8]$$

where V_c is the volume of the cavity (m^3). The yield stress used here is again enhanced by a factor of 3 to allow for the dynamic effect.

17.36 Explosion of a Cased Explosive

Another event which can give rise to missiles is the explosion of a cased explosive. This is considered in this section. Whilst the discussion has most relevance to an explosion involving munitions, there are features which have wider application.

There is obviously a large volume of work done by the military dealing with the various aspects of this problem. In particular, the accounts given in *Structural Defence* by Christopherson (1946) and in the *Textbook of Air Armaments* (referred to below as the *Textbook*) by the Ministry of Supply (1952) provide a basic starting point, though this needs to be supplemented by more recent work on the specific aspects.

A model for an exploding object which draws on this work has been given by Gilbert, Lees and Scilly (1994f,g), and the account here is based mainly on this.

In addition to the models specifically for fragments from cased explosives described below, further material on missiles is given in Section 17.34.

17.36.1 Exploding object

The exploding object primarily considered is a cased high explosive, typically a shell or bomb. The explosive could be some combination of TNT and RDX. The following treatment, therefore, is in terms of weapons.

17.36.2 Fragment mass distribution

The fragmentation behaviour of a cased explosive varies depending on the nature of the casing. A plain casing will undergo natural fragmentation. An armament such as a shell may be high explosive or shrapnel. In the latter case the casing is designed to give a particular pattern of fragments.

The fragment mass distribution of this latter type of casing is obtained experimentally by conducting an explosion and collecting the fragments formed. In some cases information is also obtained on the fall of the fragments.

Work on fragment mass distribution (FMD) includes that of Mott (1947), Held (1968, 1979, 1990), Grady (1982a,b), C.E. Anderson, Predebon and Karpp (1985), Burman (1989), Helwig, Klee and Hubner (1989) and Jagusch (1989).

An early method of representing the FMD was that of Mott (1947). That described here is the method developed by Held (1968, 1979, 1990). The correlation is

$$M(n) = M_o[1 - \exp(-Bn^\lambda)] \qquad [17.36.1]$$

where $M(n)$ is the cumulative fragment mass, or overall mass of the fragments of number n, starting with the

largest fragment, M_o is the total mass of fragments, n is the number of the nth largest fragment, or cumulative fragment number, and B and λ are constants.

The mass m of the nth fragment is obtained from Equation 17.36.1 by differentiation:

$$m = \frac{dM(n)}{dn} = M_o B\lambda n^{\lambda-1} \exp(-Bn^{\lambda}) \quad [17.36.2]$$

Held (1990) gives as an example the fragment mass distribution of the Hispanio Suiza 30 × 170 mm incendiary high explosive projectile. The parameters which he obtains for this weapon are $M_o = 288.7$ g, $B = 0.511$ and $\lambda = 0.7318$.

In some cases an improved fit for higher values of n is obtained by replacing M_o with a modified mass M_{oB} defined as that value which best fits the set of equations

$$M_{oB} = \frac{M(n)}{1 - \exp(-Bn^{\lambda})} \quad [17.36.3]$$

Equation 17.36.1 then becomes

$$M(n) = M_{oB}[1 - \exp(-B_B n^{\lambda_B})] \quad [17.36.4]$$

where B_B and λ_B are constants.

The risk from explosion of a cased explosive depends on the number and size of the fragments. As the number of fragments increases, the risk initially increases but eventually decreases as the fragments become too small to cause injury.

Often it is a stack of weapons which is of interest. Stack effects on FMD are considered in Section 17.36.11.

17.36.3 Projection angle of fragments

Methods exist for the estimation of the angle at which the fragments from a single weapon are projected. Treatments include those of Christopherson (1946), G.I. Taylor (1963a,b) and Karpp and Predebon (1974).

A discussion of the direction in which fragments are projected is given by Christopherson (1946). He states 'Fragments of the case are, in general, projected *normally* to the *inner surface* on which the pressure of the explosive gases acts *at the moment of break-up*.'

Weapons such as bombs have some curvature along their length, which tends to spread fragmentation over a wider zone. If detonated at one end the casing becomes conical rather than cylindrical, directing fragments away from the initiating end.

A study of the fragmentation of tubular bombs was conducted by G.I. Taylor (1963a,b). He gives the following equation for the angle ϕ formed by the deforming case relative to the direction of the detonation wave:

$$2 \sin \phi = u_o/D \quad [17.36.5]$$

where D is the velocity of detonation (VOD), u_o the initial velocity of the fragment (VOF), and ϕ is the angle to the axis of the tube at which fragments are projected. ϕ is known as the Taylor angle.

In practice, these models of projection angle appear of limited use in accident modelling, where the appropriate approach depends on the particular case. Considering the plan view, it will be sufficient in many scenarios to assume that for a weapon on its side, fragments of the cylindrical part of the casing are ejected in two broad sectors, whilst for a weapon standing vertically the fragments are ejected in all directions; in both cases the end cap and base can be taken as travelling along the axis of the weapon.

It is also necessary to consider the angle of elevation. In principle, for the case of an exposed person standing vertically, three cases need to be considered, as illustrated in Figure 17.103. In the near field, shown in Figure 17.103(a), the fragments hitting the human target are those projected at low angle α; the fragments approach the target with near normal incidence. In the medium field, shown in Figure 17.103(b), the target is struck by some fragments of low trajectory issuing at angle $\beta \pm \delta_1$ and others of high trajectory issuing at angle $\gamma \pm \delta_2$; in both cases the fragments approach the target obliquely. Finally, at the limit of the fragment range, shown in Figure 17.103(c), these two trajectories combine; again the fragments approach the target obliquely. This is an idealized model. In practice, due to air drag, fragments slowing below a critical velocity will tend to stall.

Frequently weapons are in an ordered stack. Alternatively, in an accident, they may be in a disordered pile. In each case there is an effect on the angle of projection. Stack effects on projection angle as discussed in Section 17.36.11.

17.36.4 Initial velocity of fragments

Methods of determining the initial velocity of the fragments from a weapon include those given in the *Textbook*, in *Structural Defence* and by Gurney (1943), V.J. Clancey (1972b), Kamlet and Finger (1979) and E. Hirsch (1986).

One approach to the estimation of the initial velocity of fragments is the use of empirical rules. The *Textbook* suggests values for the initial velocities of 4000 ft/s for bomb fragments and 3000 ft/s for shell fragments.

For fragments from the bursting of an cased TNT charge the following empirical values of initial velocity have been given by V.J. Clancey (1972b) in the context of incident investigation:

Thin case	8000 ft/s
Medium case	6000 ft/s
Thick case	2000 ft/s

This approach provides a useful guideline, but as Clancey points out, it assumes that any size charge will propel fragments the same distance, which is not the case – larger explosions tends to project fragments further.

One equation for the initial velocity of the fragments is that given in *Structural Defence* by Christopherson (1946):

$$V_o = \{8.22 \times 10^7[1 - \exp(-0.69E/C)]\}^{\frac{1}{2}} \quad [17.36.6]$$

where C is the mass of the uniform cylindrical case per unit length (lb), E is the mass of charge per unit length (lb) and V_o is the initial velocity (ft/s). Equation 17.36.6 is a generalization of an empirical equation obtained by Payman for small tetryl filled bombs. Christopherson states 'for a medium case bomb, the initial velocity of fragments will not exceed approximately 7500 ft/s.'

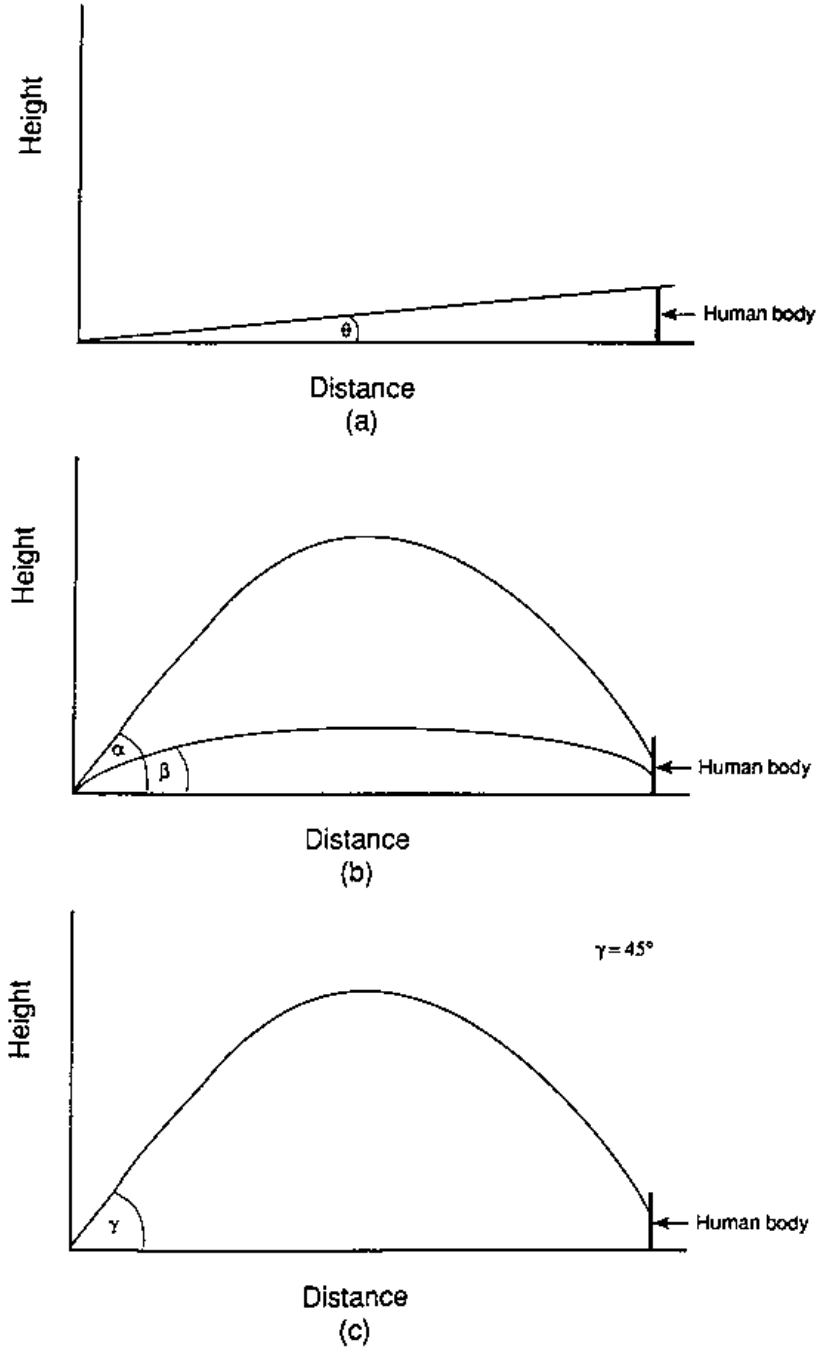


Figure 17.103 *Angle of projection in the vertical plane of missiles from a cased explosive (a) near field; (b) medium field; (c) limit of range (Gilbert, Lees and Scilly, 1994f)*

The correlation for initial velocity which appears to be most widely used is that of Gurney (1946). The Gurney model is based on a fundamental energy balance. The sum of the kinetic energy of the fragments and the energy of the expanding explosion products is equated to the internal energy of explosion. It is assumed that all the fragments are projected out at the same velocity and that the velocity of the gaseous explosion products increases from zero at the centre of the mass of the explosive out to a maximum which is also the velocity of the fragments at the moment of break-up of the casing.

The equation given by Gurney for the initial fragment velocity u_o is

$$u_o = C_G\left(\frac{C/M}{1+(C/M)/2}\right)^{\frac{1}{2}} \qquad [17.36.7]$$

with

$$C_G = [2(-\Delta E)]^{\frac{1}{2}} \qquad [17.36.8]$$

where C is the mass of explosive (kg), ΔE is the internal energy of explosion per unit mass of explosive (J/kg), M is the mass of the cylindrical section of the casing, and hence of the sidewall fragments (kg), u_o is the initial fragment velocity (m/s), and C_G is the Gurney constant (m/s). C_G is also commonly known as the Gurney velocity.

The Gurney constant is one of the standard parameters of an explosive. Values for a number of the more common explosives are given by Kinney and Graham (1985).

The use of the Gurney equation to determine the velocity of fragments from an explosion is known as a Gurney analysis. Accounts of such analysis have been given by G.E. Jones, Kennedy and Bertholf (1980) and by Kinney and Graham (1985).

Further treatments of the Gurney method have been described by Kamlet and Finger (1979) and E. Hirsch (1986). Kamlet and Finger give for the Gurney constant the following relation:

$$C_G = 0.887\phi^{0.5}\rho_o^{0.4} \qquad [17.36.9]$$

with

$$\phi = NM^{0.5}Q^{0.5} \qquad [17.36.10]$$

where C_G is the Gurney constant (km/s), M is the average molecular weight of the products of explosion, N is the number of moles of gas produced by the explosion, Q is the heat of detonation (cal/g), ρ_o is the explosive loading density (g/cm^3) and ϕ is a parameter.

Stack effects on initial velocity are considered in Section 17.36.11.

17.36.5 Flight of fragments

Treatments of the flight and retardation of fragments include those in the *Textbook* and in *Structural Defence* and by Zaker (1971) and Naz (1989).

For the retardation of fragments the *Textbook* gives

$$V = V_o\exp(-s/284m^{\frac{1}{3}}) \qquad [17.36.11]$$

where m is the mass of the fragment (oz), s is the distance travelled (ft), V is the velocity of the fragment (ft/s) and V_o is its initial velocity (ft/s).

In his account in *Structural Defence*, Christopherson states:

> Immediately after the case has broken up, the shock front expands more rapidly than the case, and thus at this stage the fragments are surrounded by air moving outwards, at a velocity comparable to their own. It is not long, however, before the rapid deceleration of the shock front due to the falling shock-wave pressure allows the fragments to overtake it and pass through it into the zone of undisturbed air beyond. As soon as this happens – and it happens within a few feet of the bomb – the fragments are retarded by a force which is proportional to the square of their velocity, and to the area presented. Under these conditions, it is easy to show that the velocity at a distance x ft from the origin is given by an equation of the form $v = Ve^{-kxA/W}$.

This latter equation is written here as

$$V = V_o\exp(-kxA/W) \qquad [17.36.12]$$

where A is the area of the fragment, V is the velocity of the fragment, V_o is the velocity of the fragment at the commencement of retardation by air drag, W is the mass of the fragment, x is the distance and k is a constant.

It should be noted that Christopherson's statement that the drag force is proportional to the square of the velocity applies to the subsonic regime only.

Christopherson quotes the following relations for the velocity of a fragment in air, based on a generalization of an equation given by Payman for tetryl-filled tubes

$$V = V_o\exp(-0.002\,04xa/w^{\frac{1}{3}}) \qquad V \geq V_s \qquad [17.36.13a]$$

$$= V_o\exp(-0.001\,37xa/w^{\frac{1}{3}}) \qquad V < V_s \qquad [17.36.13b]$$

with

$$a = A_m/Q^{\frac{2}{3}} \qquad [17.36.14]$$

where a is the dimensionless coefficient of area, A_m is the mean area presented by the fragment in flight (ft^2), Q is the fragment volume (ft^3), V is the velocity of the fragment (ft/s), V_o is the initial velocity of the fragment (ft/s), V_s is the velocity of sound (ft/s), w is the mass of the fragment (oz) and x is the distance (ft). The value quoted for the velocity of sound is 1100 ft/s.

For natural fragmentation Christopherson quotes work at the Safety in Mines Research Station to the effect that

$$a = 1.93 + 1.3w \qquad [17.36.15]$$

Christopherson states that for a cube the value of a is 1.5, but that for natural fragments it is higher. He argues that there will be very few fragments for which the term $a/w^{1/3}$ is less than 2. Equation 17.36.15 gives for $a/w^{1/3}$ a minimum value of 3.2 at $w = 0.75$ oz.

A large fragment tends to retain its velocity. Such a fragment will travel some hundreds of feet before its velocity is halved.

The model for fragment flight given by V.J. Clancey (1972b) and quoted in Section 17.34 appears very similar to that of Christopherson.

Another relation for the flight of a fragment from a weapon is that given by Naz (1989):

$$u = u_o\exp\left(-\frac{C_x}{2}\frac{A_s}{m}\rho_a x\right) \qquad [17.36.16]$$

where A_s is the effective area of the fragment (m^2), C_x is the drag coefficient, m is the mass of the fragment (kg), u is the velocity of the fragment (m/s), u_o is its initial velocity (m/s), x is the distance (m) and ρ_a is the density of air (kg/m^3).

For the effective area A_s Naz gives

$$A_s = (\pi/4)a^2 \qquad \text{Sphere} \qquad [17.36.17a]$$

$$A_s = (3/2)a^2 \qquad \text{Cube} \qquad [17.36.17b]$$

where a is the diameter of the sphere or the side of the cube (m).

For the coefficient C_x Naz gives relations from the work of Suterlin (1966), which show the coefficient for spheres, cubes and cylinders as a function of Mach number. He also quotes work by McCleskey (1988a) which shows that there is a considerable scatter in observed values of the coefficient.

17.36.6 Range of fragments

The account of fragment flight given by Christopherson in *Structural Defence* also includes a treatment of the maximum range of a fragment. From Equation 17.36.13a and taking $a/w^{\frac{1}{3}}$ as 2,

$$V = V_o \exp(-0.004\,09x) \qquad [17.36.18]$$

Then from this equation the distance at which the velocity V falls to the velocity of sound V_s is

$$x = [\ln(V_o/V_s)]/0.004\,09 \qquad [17.36.19]$$

For an initial velocity of 7500 ft/s Christopherson obtains a distance of 475 ft.

Then noting that $V = dx/dt$ and integrating Equation 17.36.18 with respect to time gives

$$x = [\ln(1 + 0.004\,09V_o t)]/0.004\,09 \qquad [17.36.20]$$

or

$$t = [\exp(0.004\,09x) - 1]/(0.004\,09V_o) \qquad [17.36.21]$$

From Equation 17.36.21 the time for transition to subsonic velocity is only 0.2 s. This is a negligible proportion of the total flight time.

Utilizing Equation 17.36.13b again with a value of the term $a/w^{\frac{1}{3}}$ of 2 and integrating as before, taking the initial velocity now as that of sound gives

$$x = [\ln(1 + 0.002\,73V_s t)]/0.002\,73 \qquad [17.36.22]$$

Christopherson obtains a maximum value of the flight time of 330 s, on the basis that the flight time is necessarily less than the flight time to maximum range in the absence of air resistance, which is $V_v/2g$, where V_v is the initial vertical velocity (ft/s), and that the value of this term for maximum range is necessarily less than $V_o/2^{\frac{1}{2}}$. Then substituting this flight time of 330 s in Equation 17.36.22 gives a travel distance of 2530 ft, which together with the distance of 475 ft travelled in the supersonic range yields for the maximum range of the fragment a total distance of 3005 ft. He compares this with the distance of 1000 yards usually taken as the danger area for a 1000 lb medium capacity (MC) bomb and comments that the latter is certainly on the safe side, though not so grossly as might be expected in view of the crudeness of the method adopted.

There is also available some empirical guidance on the range of fragments from cased explosives. The empirical correlation for the maximum horizontal range of fragments from a cased charge given by V.J. Clancey (1972b) has been described in Section 17.4.

Guidance is also available from relationships for safety distances. A formula of this type is the US safety distance in bomb disposal work. This is given by Kinney and Graham (1985), quoting Lenz (1965), as follows:

$$r = 120W^{\frac{1}{3}} \qquad [17.36.23]$$

where r is the safety distance (m) and W is the mass of explosive (kg). There is a minimum distance of 90 m. However, since this is a safety formula it may be expected to incorporate a safety factor.

17.36.7 Mean presented area of fragments

The mean presented area (MPA) of the fragments is relevant both to the their flight and to their injuring power. In the treatment just given, which is concerned with flight, the MPA is given by Equations 17.36.14 and 17.36.15.

17.36.8 Number of fragments hitting target

Following the *Textbook*, the number n of incapacitating fragments is

$$n(x) = \int_0^\infty q(v, x)r(x)\,dv \qquad [17.36.24]$$

where n is the number of incapacitating fragments, q is the number of fragments of equivalent velocity v at a distance x, r is the proportion of fragments of equivalent velocity v at a distance x capable of causing incapacitation, v is the velocity of the fragment (ft/s) and x is the distance (ft).

The density of incapacitating fragments over the area of a sphere centred on the exploding object is

$$\frac{N(x)}{A_p} = \frac{n(x)}{4\pi x^2} \qquad [17.36.25]$$

where A_p is the projected area of the exposed person (ft^2) and N is the average number of incapacitating fragments at a distance x. Hence

$$N(x) = \frac{n(x)A_p}{4\pi x^2} \qquad [17.36.26]$$

The value of the projected area A_p does not appear to be given explicitly in the *Textbook*, but a value of 2.8 ft^2 may be inferred.

The probability p of being hit by one or more incapacitating fragments is taken as given by the Poisson distribution and is therefore

$$p = 1 - \exp[-N(x)] \qquad [17.36.27]$$

A vulnerable area A_v may be defined as the equivalent ground area in which probability of incapacitation is unity. This vulnerable area is

$$A_v = \int_0^\infty p(x)x\,dx \qquad [17.36.28]$$

where A_v is the vulnerable area (ft^2).

The vulnerable area as so defined takes no account of any hard cover which may provide protection from the fragments.

The *Textbook* gives as an illustrative example the determination of the fragments from a British 20 lb bomb. The example is described by Gilbert, Lees and Scilly (1994f).

17.36.9 *Textbook* model

The model of an exploding weapon given in the *Textbook* utilizes the framework relations Equations 17.36.24–17.36.27 together with the following supporting equations. The FMD is obtained from experimental values for the particular weapon. The fragments are evidently assumed to be projected equally in all directions with an initial velocity obtained from the empirical values quoted. The flight and retardation of the fragments are given by Equation 17.36.11. As described in Section 17.42, the *Textbook* also includes an injury model.

17.36.10 Model of Gilbert, Lees and Scilly

In the model of Gilbert, Lees and Scilly (1994f) use is again made of Equations 17.36.24–17.36.27 as the framework, but with a different set of supporting relations. The FMD is based on fitting the experimental values for the weapon to Equation 17.36.1 of Held. The angles of projection in plan and elevation depend on the problem considered and guidance is given on this aspect. For the initial velocity use is made of the Gurney equation (Equation 17.36.7) with the Gurney constant given by Equation 17.36.9 of Kamlet and Finger. The flight and retardation of the fragments is described by Equation 17.36.13 of Christopherson, which covers both sonic and subsonic regimes.

The model is used in conjunction with the model for injury from penetrating fragments given by the authors and described in Section 17.42.

Gilbert, Lees and Scilly (1994g) also describe a computer program EXFRAG which gives for an exploding weapon the probability of defined degrees of injury as a function of distance and give an illustration of the results obtained.

17.36.11 Stack effects

In the foregoing treatment the exploding object is taken as a single weapon. In many situations of practical interest it is likely to be a stack of weapons. There is a potential stack effect on each of the following features: (1) the number of fragments, (2) fragment mass distribution, (3) the projection angle of the fragments and (4) the initial velocity of the fragments.

There is little published information which can be used to quantify these effects, but the following qualitative comments can be made. In a stack explosion, a significant proportion of the fragments hit other objects within the stack and do not leave the stack. This potentially affects not only the number but the mass distribution of fragments leaving the stack. The angle of projection of the fragments depends on the nature of the stack, which may be an ordered stack or a disordered pile. The former has to be dealt with on a case by case basis, whilst for the latter the common assumption is that the fragment density is the same in all directions. There may also be stack effects on the initial velocity in so far as fragments may be further accelerated by the hot gases from the explosion.

17.37 Explosion of an Explosive Load

Another situation which it may be necessary to model is the explosion of a load of condensed phase explosives, either uncased or cased. The former might typically be blasting explosives, the latter munitions.

Models for the explosion of a condensed phase explosive, particularly in a built-up area, have been given by Withers and Lees (1991) and Gilbert, Lees and Scilly (1994a–i). The model of the latter is encoded in the program EXMOD, which incorporates the program EXFRAG.

The following account of the modelling of this situation is based on the work described by the latter authors. Using appropriate physical models, it is possible to estimate as a function of distance the intensity of the various physical effects and hence, using the corresponding injury relations, the probability of defined types of injury for defined types of exposure. Then using a suitable model for the numbers with each type of exposure as a function of distance, an estimate can be made of the numbers suffering each type of injury. Where the explosion occurs not at the start but during the course of an incident, separate estimates can be made for different times into the incident.

17.37.1 Exploding object

The exploding object is envisaged as a load of explosives, typically uncased civil explosives or cased explosives in the form of munitions such as shells, bombs, etc.

17.37.2 Explosion scenario

The elements of the scenario are the events prior to the situation of imminent risk; the explosion itself; the persons at risk; the physical characteristics of the location; and the human behaviour prior to the explosion.

The most common scenario for the realization of the hazard is that of engulfment of the explosive load in a fire which lasts long enough to initiate an explosion. This scenario is important not only by virtue of its relative frequency, but also because all the features just mentioned are relevant, which is not the case for every scenario.

The approach to scenario development takes as its starting point the persons at risk, in other words the targets of the explosion. Categories of persons exposed are defined which are intended to be exhaustive over the whole course of the scenario and estimates made of the numbers in each category at the start of the scenario and of the change in these numbers with time until the explosion occurs.

If the explosion is caused by a sudden event such as impact, the start is the explosion itself. If it is caused by a more gradual event such as fire, the start is the occurrence of an event observable either by the vehicle crew or the public.

17.37.3 Explosion effects

The principal effects of a condensed phase explosion such as the explosion of a load of cased explosives on a lorry are;

(1) blast;
(2) fireball;
(3) missiles –
  (a) primary fragments,
  (b) secondary missiles;
(4) crater;
(5) building damage.

Primary fragments include those generated by the disintegration of the casing and are also taken to include those from the vehicle. Secondary fragments include fragments from the crater and objects set in motion by the blast wave, not only objects travelling in a more or less horizontal direction, but others such as glass, falling vertically. The blast wave may also cause translation of the human body, causing it to fly through the air or to tumble along the ground, and possibly to impact with some hard object.

There may also be other effects. For example, in some large explosions of explosives in ships at docks, hot fragments have been ejected which then caused secondary fires. These effects are not, however, considered in the model.

17.37.4 Population exposure

These explosion effects act on an exposed population. For this particular type of incident it is necessary to model this population in some detail. The exposure model used covers the population density, the population's disposition indoors and outdoors, the categories of exposure, the incident scenarios and the vulnerabilities of persons in each exposure category in given scenarios.

For exposure a basic distinction is between persons indoors and those outdoors, since this affects vulnerability to the individual injury mechanisms. For example, persons outdoors are more vulnerable to fragments from the casing and those indoors to building collapse.

For each of these groups further distinctions are made based on situation or behaviour. For those indoors the classification used is:

I1 Persons unaware or aware of the incident who go about their normal business
I2 Persons aware of the incident who observe it through a window (or those unaware who happen to be close to a window)

The classification used for those outdoors is:

O1 Persons on foot unaware or aware of the incident who go about their normal business
O2 Persons occupying vehicles near to the scene
O3 Persons on foot aware of the incident who have come to the scene as spectators
O4 Members of the emergency services who have come to the scene

As stated above, the numbers of persons in each category will in principle change with time, but the scope for such change will depend on the interval between the start of the scenario and the explosion.

At the start of the scenario, there are persons in categories I1, I2, O1 and O2 but, by definition, in no other category. Persons in O1 are essentially pedestrians who are passing by or gathered for some purpose such as an open market.

If the scenario takes a finite time to develop, the numbers in each indoor category may be expected to change. Persons indoors may observe the scene through windows. Alternatively, they may take evasive action against the risk of an explosion, either by moving further away or by changing posture. The number of persons in each outdoor category may also be expected to change. Some pedestrians may continue about their business, but others will take evasive action, essentially by quitting the scene. Those who by contrast are attracted to the scene are classed as spectators. Likewise, the occupants of vehicles may continue on their journey or may stay near the scene, possibly as spectators, but more probably owing to obstruction of the traffic. In due course, members of the emergency services will arrive. Thus the numbers in each category will tend to change as the scenario develops, the numbers in some categories falling and those in other categories rising. The total number exposed is not assumed to be constant; it may decrease or increase.

The model therefore gives the number of persons exposed in each category at the start of the scenario and over its course. It may be used to obtain an instantaneous picture, or 'snapshot', of these numbers at any time up to the explosion.

17.37.5 Blast

The blast effects for a condensed phase explosive used in the blast submodel are the peak incident overpressure and impulse and the peak dynamic pressure and dynamic pressure impulse, obtained from the relations given in Section 17.26.

Blast causes direct injury to the eardrum and to the lung and indirect injury by whole body displacement. Eardrum rupture is a function of peak incident overpressure. Lung injury is a function of peak incident overpressure and, for some postures, of peak dynamic pressure and of impulse. Whole body displacement is a function of peak dynamic pressure and dynamic impulse. The relevant injury relations are given in Section 17.38.

17.37.6 Fireball

The fireball from a condensed phase explosive is described by a submodel different from that for a hydrocarbon fireball. The relevant model is given in Chapter 16. Injury from the fireball occurs due to engulfment in the fireball or thermal radiation from it. It is assumed in the model that a person engulfed in the fireball is killed. The injury relations for thermal radiation are those given in Chapter 16 and are the same as those for injury by radiation from hydrocarbon fireballs or pool fires.

17.37.7 Missiles

The missile submodel treats six types of missile: (1) primary fragments from the casing, if any; (2) fragments from the vehicle; (3) fragments ejected from the crater; (4) secondary missiles set in motion by the blast; (5) falling masonry and glass; and (6) flying glass.

The prime application of these models is to persons outdoors. However, they are also applicable to persons indoors who are near windows, except that the model for falling masonry and glass is specific to persons outdoors; the effect of falling masonry on persons indoors is taken

into account in the separate housing damage model given in Section 17.39.

An outline of the model used for fragments from the casing and the vehicle has been given in Section 17.36. The models for crater ejecta and for falling masonry and glass are described in Section 17.34 and that for flying glass in Section 17.40.

No separate model is used for the effects of secondary missiles on person outdoors; the effect of such missiles indoors is taken into account in the housing damage model.

17.37.8 Building damage

The building damage submodel used is actually a housing damage model. Separate submodels for damage to, and injury in, other structures may be incorporated, but are not part of the authors' model.

Some justification for the wider use of the housing damage model is the fact that in air raids on Britain in the Second World War the overall probability of injury in other types of building happened to be similar to that in housing.

The housing damage submodel used is the correlation between category of housing damage and mass of explosive as given by the revision by Gilbert, Lees and Scilly (1994c) of the Jarrett equation. This model is described in Section 17.33.

17.37.9 Injury to persons outdoors

The model for explosion injury outdoors is therefore based on four separate broad causes of injury: (1) blast causing eardrum rupture and lung injury, (2) blast causing injury by whole body displacement, or bodily translation, (3) injury from the fireball and (4) injury from the following types of missile: (4a) primary fragments from the casing, if any, (4b) fragments from the vehicle, (4c) crater ejecta, (4d) falling masonry and glass, and (4e) flying glass. The models for injury from these various causes have just been described. The probability of injury outdoors is estimated by applying each of these submodels in turn.

The model gives the probability of lethal injury for all the injury modes mentioned; in some cases it also gives the probability of sublethal types of injury, e.g. eardrum rupture.

Allowance is made in the model for multiple injury, as described in Chapter 9 and in Section 17.38.

17.37.10 Injury to persons indoors

The model for explosion injury to person indoors is based on the correlation between category of housing damage and probability of injury described in Section 17.39.

This correlation gives the probability not only of lethal injury but also that of severe injury and of light injury.

This model for injury to persons indoors includes injury from flying glass, but, where appropriate, this latter may be accorded separate treatment, using the model for injury from flying glass given in Section 17.40.

17.37.11 Large targets

The model also includes an estimate of the probability that an explosion occurring at random in a built-up area will find a target comprising a large number of people, such as a block of flats or a large store or market. The estimate is based on the size distribution of targets hit by V-2 rockets. From these data the authors give the following estimates of incident size versus probability of occurrence:

Deaths	*Probability*
≥ 10	0.089
≥ 33	0.014

It should be borne in mind that the data include a number of cases where there was a direct hit and that the population densities in wartime London were much higher than they are today, by a factor in the range 1.5–2.

17.38 Explosion Injury to Persons Outdoors

Turning to the effects of explosions on humans, it is necessary to distinguish between effects on persons outdoors and effects on those indoors.

For persons in the open there is a large amount of information available on specific explosion injury causes and modes. Accounts are given in *The Effects of Nuclear Weapons* (Glasstone, 1962; Glasstone and Dolan, 1980) and in *Explosion Hazards and Evaluation* (W.E. Baker *et al.*, 1983).

Much of the data on injury from explosions derives from the work of Zuckerman and co-workers in the 1940s, from work on the effects of nuclear weapons described by Glasstone (1962) and Glasstone and Dolan (1980) and from an extensive programme of research at the Lovelace Foundation in the 1960s, 1970s and 1980s, which has been reported by Bowen, Fletcher, Richmond, White and other workers. Some of this latter work is listed in Appendix 28.

A set of correlations of explosion injury is given in the *Green Book*.

The causes of explosion injury to a person in the open include the following: (1) blast, (2) whole body displacement, (3) missiles, (4) thermal effects and (5) toxic effects.

The modes of explosion injury due to these causes include (1) eardrum rupture, (2) lung haemorrhage, (3) whole body displacement injury, (4) missile injury, (5) burns and (6) toxic injury.

In the case of outdoor exposure, it is generally possible to apply the injury relations for the individual physical causes, provided that where applicable due allowance is made for the effects of more than one cause.

There are several ways in which injury may be correlated. One is in terms of single values of the injurious physical effect, of which the threshold value and the value for 50% probability of injury are particularly important. Another is a probit equation, which also generally correlates the probability of injury with a single physical effect, typically overpressure. A third is in the form of a *P–I* diagram.

Data in forms such as threshold and 50% probability values are illustrated by those given in Table 17.53 from the work of Glasstone and of White.

Probit equations have been widely used to express injury relations. The use of probit equations is illustrated

Table 17.53 *Some data on the injury effects of explosions: direct blast effects*

Effect	*Effective peak overpressure*[a] (psi)		
	Duration		
	Glasstone[b]	White[c]	
	'Long'[b]	*3 ms*[c]	*400 ms*
Eardrum rupture			
Threshold	5	5	5
50% (≥ 20 years old)	15–20	15–20	15–20
50% (≤ 20 years old)	30–35		
Lung damage			
Threshold	12 (8–15)	37–49	12–15
Severe	25 (20–30)	≥98	≥37
Lethality			
Threshold	40 (30–50)	112–156	37–52
50%	62 (50–75)	156–217	52–72
100%	92 (75–115)	217–302	72–100

[a] This overpressure is described as the maximum effective overpressure. It is stated that this may be one of three defined overpressures, one of which is the maximum incident overpressure for free-stream exposure if the long axis of the subject is parallel to the direction of travel of the blast wave.
[b] Tentative criteria for some injury effects applicable to a fast-rising, long-duration overpressure (after Glasstone, 1962).
[c] Tentative criteria for some injury effects in young adults applicable to fast-rising, short- or long-duration overpressure (after C.S. White, 1968b).

by the many correlations of injury given by the Lovelace Foundation workers which are cast in this form.

The probit equation form is also that used in the vulnerability model described by Eisenberg, Lynch and Breeding (1975). Much of the data on which these relations are based derives from the work of Fugelso, Weiner and Schiffman (1972). These relations have been quite widely used, mainly for lack of other data, and some are described below, but comparison with the other relations given indicates that they generally predict considerably higher levels of injury than other work.

The third form of *P–I* diagram is illustrated by those given by W.E. Baker *et al.* (1983).

17.38.1 Eardrum rupture

The data for eardrum rupture given by Glasstone (1962) and by C.S. White (1968b) are shown in Table 17.53. Both sets of data apply to rapidly rising overpressure. In general, White distinguishes between short and long duration overpressures, but his data for eardrum rupture are identical.

Relations for eardrum rupture are given in the vulnerability model described by Eisenberg, Lynch and Breeding. They quote the following data from Fugelso, Weiner and Schiffman:

Probability of eardrum rupture (%)	*Peak overpressure* (psi)	(N/m^2)
1 (threshold)	2.4	16 500
10	2.8	19 300
50	6.3	43 500
90	12.2	84 000

They derive from these data a probit equation relating eardrum rupture to peak overpressure:

$$Y = -15.6 + 1.93 \ln p^o \qquad [17.38.1]$$

where p^o is the peak overpressure (Pa) and Y is the probit.

Eardrum rupture has been discussed by F.G. Hirsch (1968), who reviews the physiology of the ear and injury to it and summarizes the available data on the blast conditions causing rupture.

The ear responds to sound waves, and a blast wave is physically the same phenomenon. For sound waves the ear responds over the frequency range 20–20 000 Hz and at very low energy levels. It is unable, however, to respond faithfully to a pulse with a period of less than 0.3 ms, and the attempt to do so results in a single, large excursion, and it is this which causes rupture. The response is governed by the peak overpressure and the rise time of the overpressure.

Hirsch states that it has been established that there is a direct relation between peak overpressure and eardrum rupture.

He states further that there is evidence that other parameters such as rate of rise and positive and negative duration also have an influence. Rapid rise of overpressure tends to increase the probability of rupture. Hence data from loading by explosion overpressures is more applicable than data from loading by static pressures.

Zalewski (1906) performed tests in which cadavers were subjected to static pressures. He obtained a mean pressure for rupture of 22.9 psi. Zuckerman and coworkers (Blake *et al.*, 1941) did work on cadavers, but used slow rising overpressures from explosions. They found for 50% probability an overpressure of about 1 atm (14.7 psi). In other studies on air raid casualties they obtained for 50% probability of rupture a lower limit of 15 psi and an upper limit of 50 psi.

G.A. Henry (1945) studied 292 men who had been subjected to a landmine explosion, 52% of whom had suffered eardrum rupture. He estimated the overpressure as 17 psi. Other data reported on eardrum rupture are those of Vadala (1930) for anti-aircraft gun blast and those of Reider (1968) for two industrial explosions. These data have been plotted by Hirsch as shown in Figure 17.104.

Hirsch reviews the data for threshold and 50% probability of eardrum rupture and obtains for a fast rising overpressure, pulse estimates of 5 and 15 psi, respectively.

The probit equation for eardrum rupture obtained from Figure 17.104 is

$$Y = -12.6 + 1.524 \ln p^o \qquad [17.38.2]$$

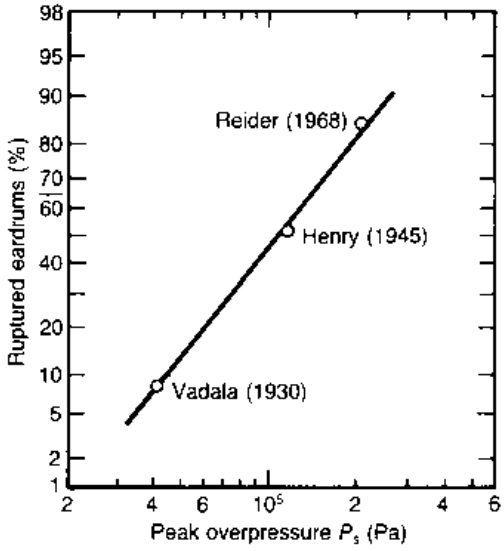


Figure 17.104 *Injury effects of explosions: eardrum rupture (after F.G. Hirsch, 1968) (Courtesy of the New York Academy of Science)*

Equation 17.38.2 is that given for eardrum rupture in the *Green Book*.

On the basis of the data given by Hirsch, W.E. Baker *et al.* (1983) have derived a *P–I* diagram for eardrum rupture. The lines for the threshold and 50% probability values are horizontal lines and correspond to peak overpressures of 5 and 15 psi, respectively.

17.38.2 Lung injury

Direct blast effects, particularly lung haemorrhage, have been studied by a number of workers, including Zuckerman (1940, 1941), Krohn, Whitteridge and Zuckerman (1942), Glasstone (1962), I.G. Bowen, Fletcher and Richmond (1968), Richmond, Damon *et al.* (1968), C.S. White (1968b) and C.S. White *et al.* (1971).

Early work on direct blast effects was carried out by Zuckerman (1940), who combined experimentation on the exposure of tethered goats to explosions with analysis of air raid casualties. In the experiments he used 70 lb charges, giving an overpressure of about 15 psi at 30 ft with a duration time of about 5 ms. Zuckerman estimated that for a 500 lb bomb the lethal overpressure for man is between 400 and 500 psi (27.6 and 34.5 bar).

The data of Glasstone and of White are shown in Table 17.53. These data indicate for long overpressure pulses a 50% lethality at an overpressure of about 60 psi (4.1 bar), but for short pulses much higher values of overpressure.

Work by Withers and Lees (1991) suggests that the overpressure for 50% lethality increases from about 10 bar for charges of 10 kg TNT to 4 bar for charges of 1000 te TNT.

Relations for death due primarily to lung haemorrhage are given in the vulnerability model by Eisenberg, Lynch and Breeding. They quote the following data from Fugelso, Weiner and Schiffman:

Probability of fatality (%)	*Peak overpressure*	
	(psi)	(N/m^2)
1 (threshold)	14.5	100 000
10	17.5	120 000
50	20.5	140 000
90	25.5	175 000
99	29.0	200 000

They derive from these data a probit equating relating death primarily from lung haemorrhage to peak overpressure:

$$Y = -77.1 + 6.91 \ln p^{o} \qquad [17.38.3]$$

Extensive work on direct blast effects was conducted in the 1950s and 1960s at the Lovelace Foundation and has been reported by Bowen, Fletcher, Richmond, White and co-workers (e.g. I.G. Bowen, Fletcher and Richmond, 1968; Richmond, Damon *et al.*, 1968; C.S. White *et al.* 1971).

This work has yielded a large amount of data on blast effects. The effects were studied for a variety of positions of the subject (standing, lying, etc.) and of situations of the subject (free stream, near wall, etc.). It was therefore necessary to correlate the results not only in terms of the peak incident overpressure, but of various peak reflected overpressures.

I.G. Bowen, Fletcher and Richmond (1968) distinguish between the cases shown in Figure 17.105. Figure 17.105(a) shows the case where the longitudinal axis of the body lies in the direction of the shock wave. For this case the peak applicable overpressure is

$$p_a^{o} = p^{o} \qquad [17.38.4]$$

where p^{o} is the peak incident overpressure (Pa) and $p_a{}^{o}$ is the peak applicable overpressure for lung injury (Pa). In Figure 17.105(b) the longitudinal axis of the body is perpendicular to the shock wave. The peak applicable overpressure is in this case

$$p_a^{o} = p^{o} + q^{o} \qquad [17.38.5]$$

where q^{o} is the peak dynamic pressure (Pa). The case where the body is in any arbitrary position in front of a surface on which the shock wave reflects is shown in Figure 17.105(c). In this case the peak applicable overpressure is

$$p_a^{o} = p_r^{o} \qquad [17.38.6]$$

where $p_r{}^{o}$ is the peak reflected overpressure. Expressions for the peak dynamic pressure and peak reflected overpressure are given in Equations 17.25.5 and 17.25.7, respectively.

One of the correlations for lung injury caused by the peak applicable overpressure is shown Figure 17.106.

These injury relations have been converted by W.E. Baker *et al.* (1983) to the alternative form of a *P–I* diagram as shown in Figure 17.107. The definition of the scaled peak applicable overpressure and scaled impulse for use in this figure are

$$\bar{p}_a^{o} = \frac{p_a^{o}}{p_a} \qquad [17.38.7]$$

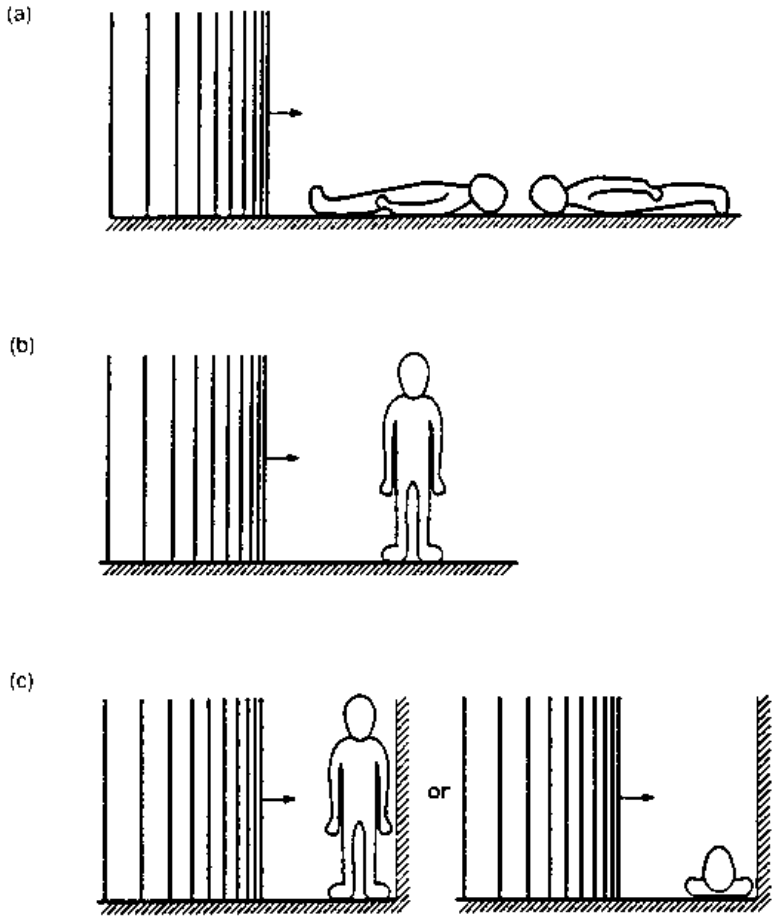


Figure 17.105 *Injury effects of explosions – postures determining lung injury (I.G. Bowen, Fletcher and Richmond, 1968): (a) long axis of body parallel to the direction of the blast wave; (b) long axis of body perpendicular to the direction of the blast wave; (c) thorax near a surface against which the blast wave reflects at normal incidence*

$$\bar{i} = \frac{i}{p_a^{\frac{1}{3}} m^{\frac{1}{3}}} \qquad [17.38.8]$$

where i is the impulse (Pa s), $\bar{i}$ is the scaled impulse ($Pa^{\frac{1}{3}}$ s/$kg^{\frac{1}{3}}$), m is the mass of the body (kg), p_a is atmospheric pressure (Pa), and $\bar{p}_a{}^o$ is the scaled peak applicable overpressure. These authors recommend the following values for body mass: babies 5 kg, small children 25 kg, adult women 55 kg and adult men 70 kg.

These correlations of Bowen, Fletcher and Richmond and of Baker *et al.* are referred to in the Green Book, which gives a PI diagram broadly similar to Figure 17.107 together with the following associated probit equation:

$$Y = 5 - 5.74 \ln S \qquad [17.38.9]$$

with

$$S = \frac{4.2}{\bar{p}_a^o} + \frac{1.3}{\bar{i}} \qquad [17.38.10]$$

where S is a 'damage number' and Y the probit for fatal injury.

17.38.3 Whole body displacement

Another blast effect is bodily translation, or whole body displacement. Accounts of whole body displacement are given by Glasstone (1962), Clemedson, Hellstrom and Lindgren (1968), C.S. White (1968b, 1971), Richmond and Fletcher (1971), W.E. Baker *et al.* (1983), Hadjipavlou and Carr-Hill (1986) and in the *Green Book*.

The data of Glasstone (1962), Clemedson, Hellstrom and Lindgren (1968), C.S. White (1968b, 1971) and Richmond and Fletcher (1971) are shown in Table 17.54.

The treatment for body translation in the vulnerability model by Eisenberg, Lynch and Breeding is somewhat complex. They derive a probit equation relating lethality for body translation to impulse:

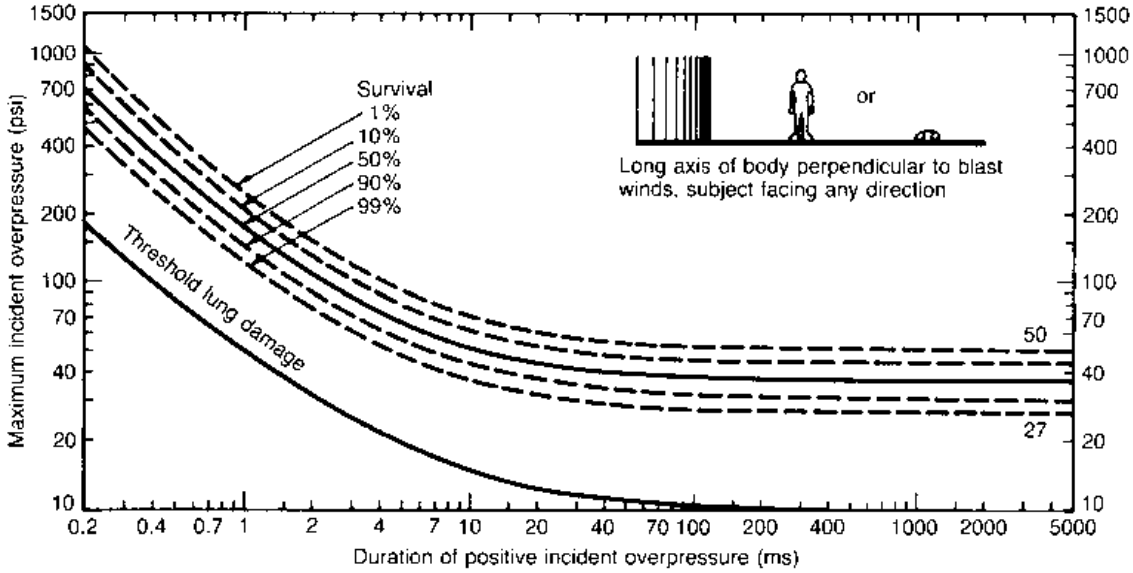


Figure 17.106 *Injury effects of explosions: lung injury – 1 (I.G. Bowen, Fletcher and Richmond, 1968). Survival curves for a 70 kg man in a free-stream situation with the long axis of the body perpendicular to the direction of the blast wave*

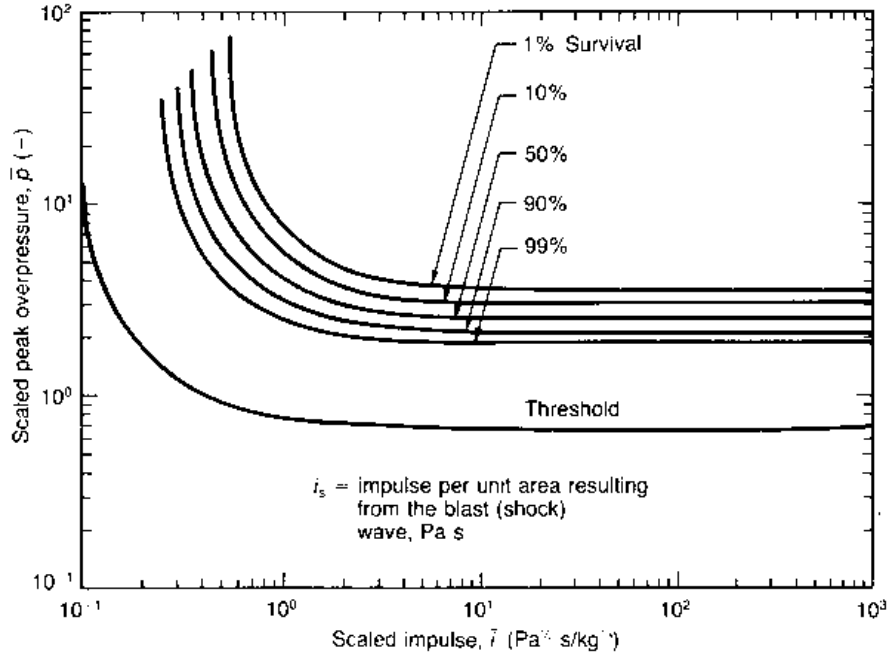


Figure 17.107 *Injury effects of explosions: lung injury – 2 (W.E. Baker et al., 1983). P–I diagram for survival applicable to all three standard postures and to different body weights (see text) (Reproduced by permission of Elsevier Science Publishers)*

Table 17.54 *Some data on the injury effects of explosions: whole body displacement*

A Data in terms of body velocity (Glasstone, 1962)

	Impact velocity	
	(ft/s)	(m/s)
Standing stiff legged impact		
Mostly 'safe':		
No significant effect	<8	<2.44
Severe discomfort	8–10	2.44–3.05
Injury:		
Threshold	10–12	3.05–3.7
Fracture threshold (heels, feet, legs)	13–16	4.0–4.9
Seated impact		
Mostly 'safe':		
No significant effect	<8	<2.44
Severe discomfort	8–14	2.44–4.3
Injury:		
Threshold	15–26	4.6–7.9
Skull fracture:[a]		
Mostly 'safe'	10	3.0
Threshold	13	4.0
50%	18	5.5
Near 100%	23	7.0
Total body impact:[b]		
Mostly 'safe'	0	3.0
Lethality threshold	21	6.4
Lethality 50%	54	16.5
Lethality near 100%	138	42

B Data in terms of dynamic impulse (Richmond and Fletcher, 1971)

	Dynamic pressure impulse (psi ms)	*Peak horizontal body velocity*	
		(ft/s)	(m/s)
No personnel blowdown	1.25	0.3	0.092
50% personnel blowdown	8.3	2.0	0.61
1% serious injury from being blown down[c]	54	13	4.0

[a] Data quoted by Clemedson, Hellstrom and Lindgren (1968); C.S. White (1968b, 1971).
[b] Earlier data were given by C.S. White (1968b). The values given here are later, revised values given by C.S. White (1971).
[c] Serious injury such as bone fracture or rupture of internal organs could occur from impact with the ground; high probability of minor injuries such as bruises and lacerations.

$$Y = -46.1 + 4.82 \ln J \qquad [17.38.11]$$

with

$$J = \int_0^{t_d} p(t)\, \mathrm{d}t \qquad [17.38.12]$$

where J is the impulse (Pa s), p is the incident overpressure (Pa) and t_d is the duration time (s). They also derive a probit equation relating serious injury for body translation to impulse:

$$Y = -39.1 + 4.45 \ln J \qquad [17.38.13]$$

A fundamental treatment of whole body displacement of a person standing involves consideration of the following effects: (1) displacement from the upright to the prone posture, (2) bodily translation followed by impact of the skull, (3) bodily translation followed by impact of the whole body and (4) tumbling across open terrain, or decelerative tumbling. In the first three cases, injury is due mainly to impact, whilst in the fourth flailing of the limbs is a significant contributor.

Considering these effects in turn, the treatment of displacement from upright is broadly as follows. It is first necessary to consider the force acting on the body. An account of the force acting on structures and objects of different configurations is given in Section 17.32. If the human body is treated like an element in an open structure, the relevant force is that due to the dynamic pressure. Then the force acting on the body initially is

$$F = C_D q^o A \qquad [17.38.14]$$

where A is the projected area of the body (m^2), C_D is the drag coefficient and F is the force acting on the body (N). The dynamic pressure decays from the peak dynamic pressure to zero over the period of the dynamic pressure duration t_q. Assuming that the shape of the dynamic pressure impulse i_q can be approximated by a triangle,

$$i_q = \frac{1}{2} q^o t_q \qquad [17.38.15]$$

where i_q is the dynamic pressure impulse (Pa s) and t_q is the dynamic pressure duration (s). Neglecting deceleration, the velocity u attained by a body of mass m due to this impulse is given by

$$mV = \frac{Ft_q}{2} \qquad [17.38.16]$$

where m is the mass of the body (kg) and V is the velocity imparted to the body (m/s).

Relations for the peak dynamic pressure and dynamic pressure impulse are given in Section 17.25. These in combination with the equations just given allow the velocity imparted to the body to be estimated.

A more refined model for bodily translation is given by Hadjipavlou and Carr-Hill (1986), which they term the 'centre-of-mass' model. This model is

$$\frac{d^2x}{dt^2} = \alpha L(t) - F(t) \qquad [17.38.17]$$

with

$$\frac{dx}{dt} = V \qquad [17.38.18]$$

$$\alpha = \frac{AC_D}{M} \qquad [17.38.19]$$

$$L(t) = P_e(t) \qquad [17.38.20]$$

where A is the projected area of the body (ft^2), C_D is the drag coefficient, F is the deceleration due to friction (ft/s^2), L is the loading on the body (lb_f), M is the mass of the body (lb), P_e is the effective pressure on the body (lb_f/ft^2), t is the time (s), V is the velocity of the body (ft/s), x is the distance travelled by the body (ft) and α is the acceleration coefficient (ft^2/lb).

The authors use for the loading an effective pressure which includes an overpressure as well as a dynamic pressure term. They give values of the acceleration coefficient α for a number of postures. That for a person standing with the body square on to the blast wave is 0.052 ft^2/lb. Then from Equation 17.38.19 for a body area A of 8.9 ft^2 and mass M of 165 lb, the corresponding value of the drag coefficient C_D is about 1.0. They quote for the deceleration of the body the following equation of E.R. Fletcher and Bowen (1968):

$$F(t) = 8.9V(t)^{0.383} \qquad [17.38.21]$$

This centre-of-mass model may be rewritten as

$$m\frac{dV}{dt} + m\phi_{fr}(t) = L(t) \qquad [17.38.22]$$

where L is the loading (N), m is the mass of the body (kg), t is the time (s), V is the velocity of displacement (m/s) and ϕ_{fr} is the deceleration due to friction (m/s^2). If the load is taken as due only to the dynamic pressure

$$L(t) = C_D q(t) \qquad [17.38.23]$$

The deceleration term is obtained, with suitable change of units, from Equation 17.38.21.

Hadjipavlou and Carr-Hill give an extensive treatment of the velocity attained by a body subject to a blast wave.

The injury effects arising from whole body displacement may then be determined from the data given in Table 17.54.

Several authors have given probit equations for such injury effects. For lethal injury due to body translation with impact of the skull on a hard surface the following equation is given by Hadjipavlou and Carr-Hill (1986) based on the data of Gurdjian, Webster and Lissner (1949):

$$Y = -6.04 + 7.11 \ln V \qquad [17.38.24]$$

where V is the velocity of the body (m/s). For lethal injury due to body translation with impact of the whole body on a hard surface, R.K. Jones, Richmond and Fletcher (1969) give

$$Y = -2.14 + 2.54 \ln V \qquad [17.38.25]$$

E.R. Fletcher, Yelverton *et al.* (1975) also give an equation for serious injury due to impact on a hard surface:

$$Y = 0.82 + 2.697 \ln V \qquad [17.38.26]$$

The basis of this equation is unclear, but it is suggested by Hadjipavlou and Carr-Hill that it is appears to be based on Equation 17.38.25 of Jones, Richmond and Fletcher with a reduction in the severity of the effect considered and a corresponding reduction in velocity.

A treatment of injury by whole body displacement is given by W.E. Baker *et al.* (1983) utilizing *P–I* diagrams.

The *Green Book* gives the following equations for lethal injury due to body displacement followed by impact with a hard surface. For skull impact

$$Y = 5 - 8.49 \ln S \qquad [17.38.27]$$

with

$$S = \frac{2.43 \times 10^3}{p^o} + \frac{4 \times 10^8}{p^o i} \qquad p^o < 4 \times 10^5 \qquad [17.38.28]$$

where i is the overpressure impulse (Pa s), p^o is the peak incident overpressure (Pa) and S is an injury factor. For whole body impact

$$Y = 5 - 2.44 \ln S \qquad [17.38.29]$$

with

$$S = \frac{7.38 \times 10^3}{p^o} + \frac{1.3 \times 10^9}{p^o i} \qquad p^o < 4 \times 10^5 \qquad [17.38.30]$$

The *Green Book* also gives the corresponding *P–I* diagrams.

Turning to decelerative tumbling, Glasstone (1962) describes experimental work in which cadavers of several animal species, including sheep and goats, were dropped from the back of a vehicle travelling at speeds

of between 10 and 60 mph (4.5 to 27 m/s). All the animals assumed a rolling posture along their long axis regardless of initial orientation. One conclusion of this work was that a person tumbling over a smooth surface might survive even if the initial velocity were high provided head injury and flailing of the limbs were avoided. Another was that injury is likely to result not so much from the initial impact of the blast wave as from impact of the body with a hard object in its path.

Glasstone gives a graph for 50% casualties in decelerative tumbling over (a) open terrain and (b) terrain with structures for a 1 kt explosion. Casualties of 50% occur at 550 ft (168 m) and 680 ft (207 m), respectively. He also proposes the scaling law

$$d = d_r W^{0.4} \qquad [17.38.31a]$$

where d is the distance for 50% casualties (ft), d_r is the distance for 50% casualties for a 1 kt explosion (ft) and W is the yield of a nuclear explosion (kt). Taking the nominal TNT equivalent yield as half that of the nominal nuclear yield, Equation 17.38.31a may be rewritten as

$$d = d_r W^{0.4} \qquad [17.38.31b]$$

where d is the distance for 50% casualties (m), d_r is the distance for 50% casualties for a 1 kte TNT explosion and W is the mass of explosive (te). Equation 17.38.31b gives for this size of explosion a 50% probability of casualty at 222 and 274 m for open terrain and terrain with structures, respectively.

E.R. Fletcher and Bowen (1968) have given for the decay of velocity in decelerative tumbling Equation 17.38.21 above.

An alternative treatment is that described by W.E. Baker *et al.* (1983). The work of W.E. Baker *et al.* (1975) is used to predict the translation velocity of the human body, the correlation being in the form of a *P–I* diagram with translational velocity as the parameter. Use is then made of data on the relation between level of injury and impact velocity given by Clemedson, Hellstrom and Lindgren (1968) and by C.S. White (1968b, 1971) as shown in Table 17.54. The authors state that there is some debate as to whether skull fracture or whole body injury is the more important. They therefore present data for both injury modes.

17.38.4 Flying glass

Blast generates missiles, the main type of missiles considered in treatments of blast injury being fragments of flying glass. The injury caused by flying glass is considered in Section 17.40.

17.38.5 Thermal and toxic effects

An explosion, like a fire, gives rise to thermal and toxic effects. These effects have been dealt with in Chapter 16 on fire and are not considered further here.

17.38.6 Distribution of injury modes

The correlations just given may be used to obtain an estimate of the relative probabilities of injury in the different modes, or injury mode distribution. The distribution of injury modes for both outdoor and indoor exposure is considered in Section 17.39.

17.38.7 Combination of injury effects

In some cases there are finite probabilities of injury in more than one injury mode and/or injury by more than one item within a given mode. For example, a person may be exposed to injury by blast and by missiles. He or she may also be exposed to injury by several items within one mode such as multiple fragments or different toxic gases.

The problem of multiple injuries and of double counting of injuries, including injuries from explosions, is discussed in Chapter 9.

17.39 Explosion Injury to Persons Indoors

For persons indoors, information on the specific explosion injury causes and modes applicable to persons in the open has some limited use, but for the most part it is necessary to rely on the correlation of injury with damage to structures, principally housing. Accounts of the latter are given in the *Green Book* and by Withers and Lees (1991) and Gilbert, Scilly and Lees (1994h).

The causes of explosion injury to a person indoors include those causing injury to a person in the open, namely (1) blast, (2) whole body displacement, (3) missiles, (4) thermal effects and (5) toxic effects, but in addition (6) falling masonry and (7) asphyxiating dust.

There are also certain differences between the outdoor and indoor situations which modify the effect of some of these causes. Indoors the distances which the body can travel before impact are short and there are many more objects which can become missiles, including walls and windows.

The modes of explosion injury due to these causes include, for the causes common to outdoors and indoors, (1) eardrum rupture, (2) lung haemorrhage, (3) whole body displacement injury, (4) missiles injury, (5) burns and (6) toxic injury and, for those specific to indoors, (7) crushing and (8) asphyxiation.

A large proportion of indoor casualties are due to the two causes specific to the indoor situation, falling masonry and asphyxiating dust, and a large proportion of the casualties are therefore in the two injury modes of crushing and asphyxiation. Injury due to these two causes, and in these two modes, is difficult to model by any means other than by correlation with structural damage.

17.39.1 Models based on housing damage

Hence for the indoor situation the prime approach to estimation of injury is by correlation with structural damage. This may be complemented to some degree by appropriate application of the outdoor injury correlations.

It is convenient here to base the treatment on damage to, and injury to persons in, housing, followed by some limited discussion of the treatment for other structures.

Withers and Lees (1991) have analysed various events which have caused housing damage and associated fatalities, including tornadoes, earthquakes, air raids, and chemical and gas explosions. They utilize two categories of injury. Primary injuries are those due to blast effects other than housing damage such as lung haemorrhage, whole body displacement, etc., and secondary injuries those due to housing damage such as

falling masonry and asphyxiating dust. They define an additional category of housing damage U, uninhabitable, which is intermediate between the Cb and Ca damage categories. By reference to the original Jarrett equation, Equation 17.33.2, for which in British units the values of the constant k are 24 for Cb damage and 70 for Ca damage, they give a value of 33 for U damage. They estimate the number of fatalities by determining the area within the U damage circle and then taking a fatality rate of 0.1 persons per house, based on an occupancy of 2.5 persons/house. Some results given by their model for an explosion of TNT occurring at random and without warning in a built-up area are:

Mass of explosive (te)	*Primary fatalities*	*Secondary fatalities*	*Total fatalities*
10^{-2}	0.07	0.009	0.079
10^{-1}	0.45	0.19	0.62
1	2.46	3.9	6.2
10	11.3	33	44
100	80.4	186	263

Gilbert, Lees and Scilly (1994h) give a model for several different degrees of injury which they define as follows: K, killed; SI, serious hospital casualty; LI, slight hospital casualty; and U, no injury requiring hospital treatment. They also define the following probabilities of injury: P(K) probability of fatal injury, P(K + SI) probability of fatal or serious injury and P(K + SI + LI) probability of fatal, serious or light injury. Further, they subdivide the A housing damage category into two further categories, Ab and Aa, where Ab corresponds to complete demolition and Aa almost complete demolition. Then to obtain the numbers with each degree of injury they utilize their revised Jarrett equation, Equation 17.33.2 again, but with the revised values of the constant k, to determine the housing damage and the correlation given in Table 17.55 for injury as a function of housing damage. The latter is based on data giving the probabilities of injury in 12 V-2 rocket incidents.

Figure 17.108 shows the number of casualties predicted by the model of Gilbert, Lees and Scilly for the explosion of a charge of TNT located at random on a built-up area with a population density of 4000 persons/km^2.

Table 17.55 *Injury as a function of housing damage for a condensed phase explosion occurring at random and without warning in a built-up area (Gilbert, Lees and Scilly, 1994h)*

Housing damage category	*Probability of injury*		
	P*(K)*	P*(K + SI)*	P*(K + SI + LI)*
Aa	0.96	1.0	1.0
Ab	0.57	0.66	0.82
A	0.62	0.71	0.84
B	0.086	0.15	0.38
Cb	0.009	0.043	0.13
Ca	0	0.002	0.006
D	0	0	0

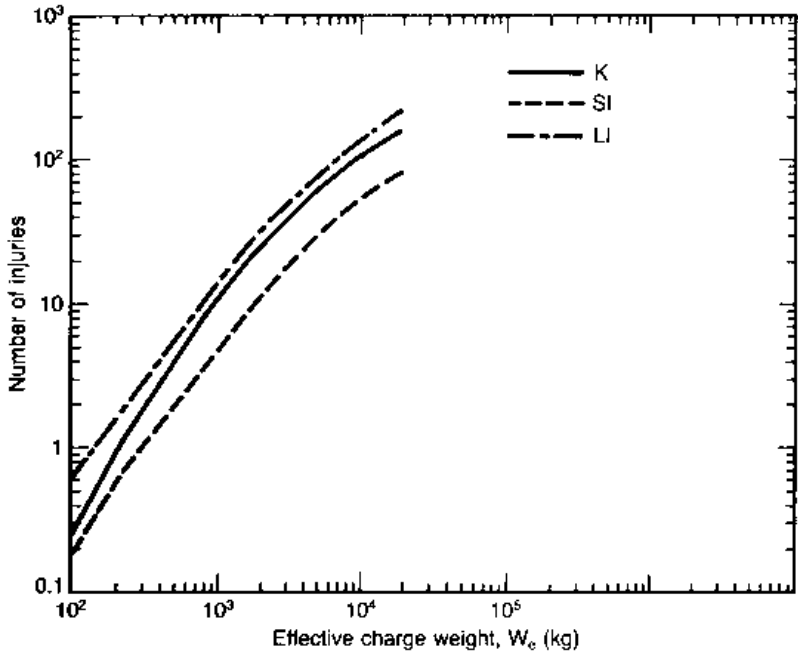


Figure 17.108 *Injury effects of explosions: number of injuries from explosion of a condensed phase explosive in a built-up area (Gilbert, Lees and Scilly, 1994h). Total injuries indoors and outdoors. Charge located in area at random. Population density 4000 persons/km^2. K, killed; SI, seriously injured; LI, lightly injured*

Table 17.56 *Distribution of injuries in casualties requiring surgery[a] admitted to a London hospital during the V-1 flying bomb raids (after R.C. Bell, 1944) (Courtesy of the* British Medical Journal*)*

	Cases		*Deaths*	
	No.	%	*No.*	%
Glass	100	47.4	1	6.3
Bomb splinters	24	11.4	3	18.7
Masonry	52	24.6	9	56.2
Blast	26	12.3	2	12.5
Burns	9	4.3	1	6.3
Total surgical	211			

[a] There were 259 casualties admitted, but some are classified in more than one category, so that there were 211 surgical cases

By comparison with a load on a road vehicle, for which in most instances the road and its verges provide a degree of separation, the figures overestimate the casualties.

The treatment of injury due to building damage in the *Green Book* refers to building collapse and is based primarily on information relating injury to building collapse in earthquakes. It refers to the work of Blume (1971), who estimates that building collapse in an earthquake results in the death of 50% of the occupants, and to that of the US Department of Commerce (1973), which gives for these circumstances an estimate of 20% dead and 80% injured. The authors of the *Green Book* conclude from these and other data that building collapse in an earthquake causes between 20 and 50% dead and adopt the same figures for explosions. Building collapse is not defined, at least not at this point in the text.

It may be noted that the estimates of the *Green Book* and of the model of Gilbert, Scilly and Lees become consistent if building collapse is taken as a degree of

Table 17.57 *Causes and modes of injury (proportion, %) by bombs in Second World War air raids (Ministry of Supply, 1952)*

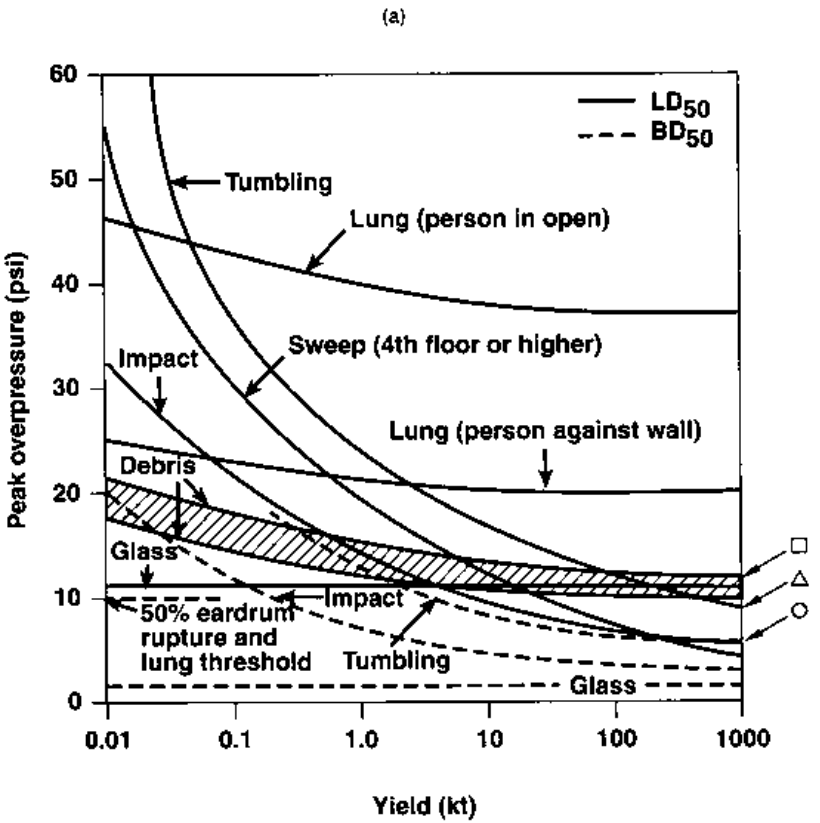
A Injury causes[a]

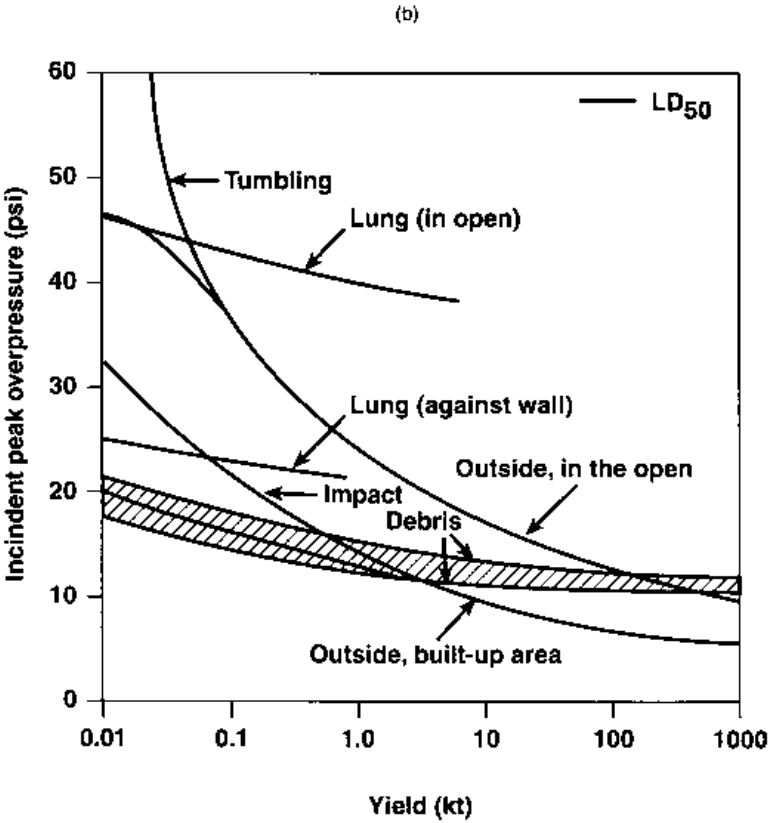
	In dwellings			*Outdoors*			*All exposures*		
	Fatal	*Hospitalizing*	*Total*	*Fatal*	*Hospitalizing*	*Total*	*Fatal*	*Hospitalizing*	*Total*
Bomb fragments	14.1	4.7	9.1	38.5	32.8	34.9	19.7	13.7	16.3
Burns	2.7	1.2	1.9	4.4	1.1	2.4	3.8	1.5	2.5
Blast	2.4	0.2	1.3	1.3	0.2	0.6	1.8	0.2	0.9
Flying glass	0.2	10.6	5.8	0	2.7	1.7	0.4	6.2	3.7
Flying debris	16.3	19.5	18.0	17.6	32.6	26.9	16.0	24.2	20.6
Falling debris	46.1	45.4	45.7	10.9	7.3	8.7	36.0	34.5	35.2
Falls, etc.	5.8	11.7	8.9	13.5	19.0	16.9	9.5	13.8	11.9
Other/unknown	12.3	6.6	9.2	13.8	4.2	7.9	12.9	5.8	8.9
Total injuries	439	498	937	160	261	421	850	1117	1967
Total casualties	353	303	656	122	159	281	680	684	1364

B Injury modes

	In dwellings		*Outdoors*		*All exposures*	
	Fatal	*Non-fatal*	*Fatal*	*Non-fatal*	*Fatal*	*Non-fatal*
Asphyxia	21	–	4	–	17	–
Gross injuries[a]	20	1.5	17.5	1.6	18	1
Penetrating injuries	9	24	22	47	11	30
Fractures	19	50	28.5	38	23	47.2
Crush injuries	14	1.6	9	0.8	12	1
Bruises/abrasions	–	8	–	4	–	4.4
Eye injuries	–	5	–	2	–	5
Other/unknown	17	9	19	8.2	19	11
Total injuries	439	196	158	126	850	483
Total casualties	353	122	122	77	680	306

[a] Gross injuries include cases where the victim was blown to bits.


(a)
Peak overpressure (psi)
60
50
40
30
20
10
0
LD50
BD50
Tumbling
Lung (person in open)
Sweep (4th floor or higher)
Impact
Lung (person against wall)
Debris
Glass
Impact
50% eardrum rupture and lung threshold
Tumbling
Glass
0.01
0.1
1.0
10
100
1000
Yield (kt)


(b)
Incindent peak overpressure (psi)
60
50
40
30
20
10
0
LD50
Tumbling
Lung (in open)
Lung (against wall)
Outside, in the open
Impact
Debris
Outside, built-up area
0.01
0.1
1.0
10
100
1000
Yield (kt)

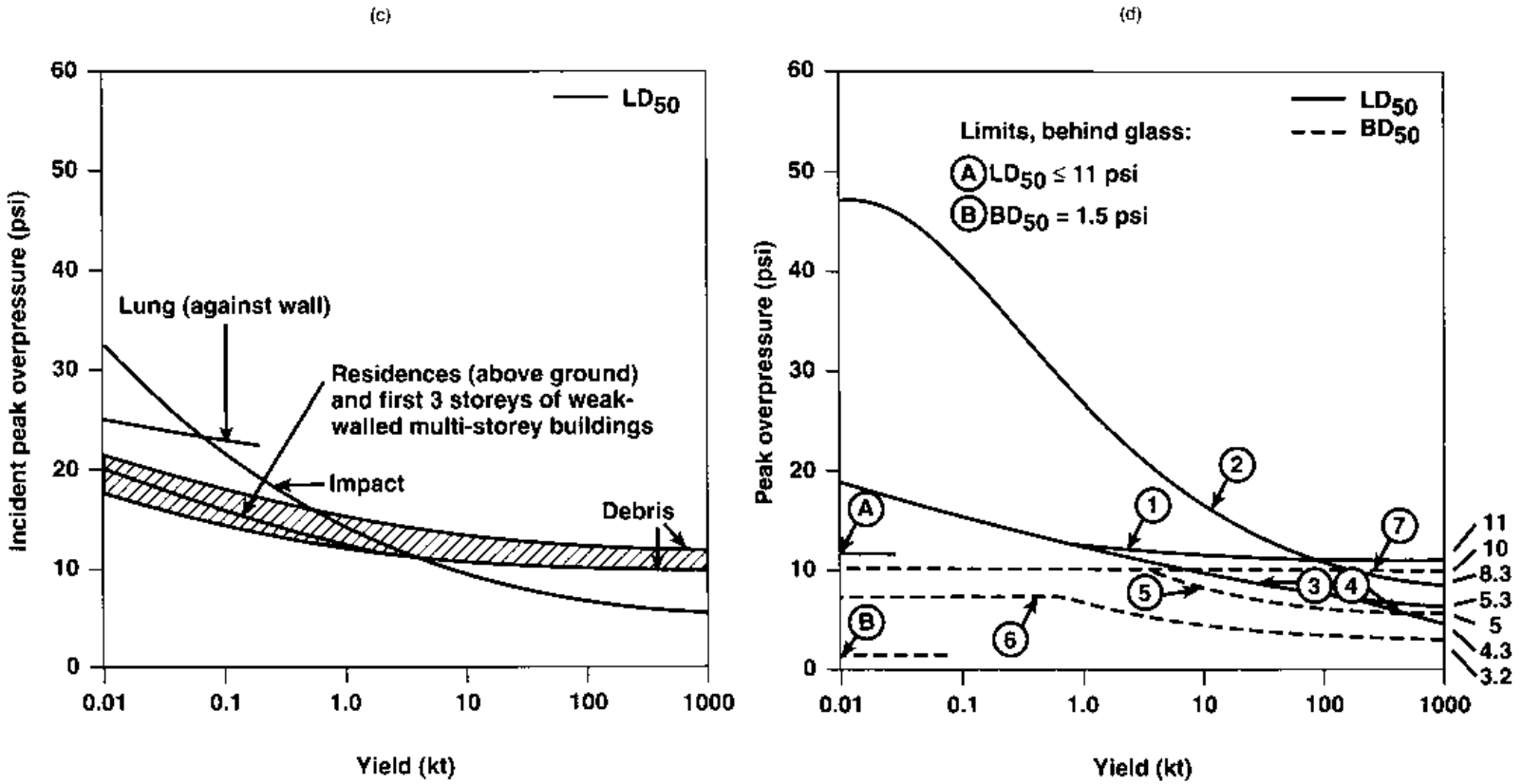


Figure 17.109 *Injury effects of explosions: lethal effects of low yield nuclear explosions (see text) (Fricke, 1975) BD_{50}, LD_{50}, load for 50% probability of burdening, lethal injury, respectively. Figure 17.109(a): ○, LD_{50} for first three floors of buildings with weak walls, brick buildings and residences. △, LD_{50} for basements of wood-frame and brick-veneer residences; basements of steel and reinforced concrete framed buildings with flat plate ground floor. □, LD_{50} for first three floors of buildings with `strong walls'; basements and sub-basements of steel and reinforced concrete framed buildings having flat slab or slab and beam ground floor construction. Figure 17.109(d): 1, home basements; basements and sub-basements of multi-storey buildings; first three floors of strong-walled multi-storey buildings. 2, outside, in the open. 3, outside, built-up area; residences, above ground; first three floors of weak-walled multi-storey buildings. 4, fourth or higher floors of multi-storey buildings. 5, outside, in the open. 6, outside, built-up area; residences, above ground; multi-storey buildings, above ground. 7, basements*

housing damage somewhat more severe than A category but much less severe than B category damage.

17.39.2 Injury inside other structures

The models just described refer to housing. The data which might allow an equivalent assessment to be made for exposure inside other structures do not appear to exist as such. However, there is some evidence that the risk in structures other than housing, taken as a whole, is similar to that in housing.

Information on the casualty rate in Britain in the Second World War was expressed in terms of standardized casualty rates. One such was the Standardized Killed and Hospitalized Casualty Rate (SKHCR). The following data are given in the *Textbook* for all weapons used in air raids:

	In open	*In dwellings*	*In other buildings*	*In shelters*	*All exposures*
SKHCR	18.85	5.31	5.45	1.94	5.07
Ratio	3.55	1.00	1.03	0.37	0.95

where the ratio is that of the SKHCR in question to the SKHCR for dwellings.

17.39.3 Distribution of injury modes

There is available some information on the distribution of injury modes from explosions for persons outdoor and indoors.

There are available a number of accounts of the casualties from explosions, both military and industrial. Descriptions of the casualties admitted to individual hospitals in the Emergency Medical Services (EMS) system for handling air raid casualties have been given by Payne (1941) for bomber raids and by R.C. Bell (1944) for V-1 flying bomb raids.

Bell gives an analysis of 259 flying bomb casualties. The breakdown of injuries is shown in Table 17.56. Some of the casualties had more than one type of injury so that the total number of entries is greater than 259. Theatre treatment was required in 83 cases.

Although these air raid data provide an indication of the injury modes, there are inevitable biases. They usually exclude casualties who died on the spot, including those who died from asphyxiation by fumes and dusts.

More detailed information is given in the *Textbook*. Table 17.57 gives a breakdown of injuries to persons outdoors and persons indoors and overall, by cause in section A and by mode in section B. The data in Table 17.57 show that a large proportion of injuries indoors were caused by falling debris and asphyxiating dust.

A study of 81 chemical and gas accidents has been described by Settles (1968). Of these, 44 involved fire and explosion, 23 fire only and 14 a detonation reaction. Settles states

> The 14 accidents in which detonating forces were present resulted in injuries to 35 persons and 34 fatalities. It appears from information available that only one of these 34 deaths resulted from blast overpressures that are associated with a detonating reaction. However, this one fatality was not the result of blast damage to human tissue. Rather, the blast pressure caused this individual to be propelled as a projectile. The other 33 persons who died in these 14 accidents were located at points where the density of flying fragments and in some cases, the lethal searing of radiant heat, were so great that their deaths were certain, even though there were no blast effects.

17.39.4 Models based on injury modes

An alternative approach to models based on housing damage is to try to estimate the overall probability of injury from the individual modes. Correlations for injury to persons outdoors which may be relevant here are those for lung haemorrhage, whole body displacement injury, missile injury, including that from flying glass, and thermal and toxic injury. However, models are lacking for two of the principal modes, crushing and asphyxiation. This makes it difficult to construct a satisfactory model of indoor injury in this way.

17.39.5 Models based on total injury

The foregoing account has given information on individual modes of injury. Studies have also been done to assist in the determination of total injury by all modes.

Rausch, Eisenberg and Lynch (1977) have described studies in support of the vulnerability model in which an attempt has been made to assess total injury. They deal in particular with the disintegration of walls and the resultant flying debris, other flying objects and bodily translation. They also refer in particular to work by Longinow *et al.* (1973) and by Fricke (1975) on injury from nuclear explosions and from low yield nuclear explosions, respectively. These authors have studied total injury by all the principal modes for people in the open and indoors in various types of building. The work on low yield explosions is of particular relevance and although the work was classified some information was released.

The estimates of the overpressures associated with 50% probability of fatality for people outdoors and indoors for such low yield explosions are shown in Figure 17.109. The yields are for nuclear weapons and should be divided by two to obtain the TNT equivalent. Figure 17.109(a) shows the basic injury mode curves from which the other graphs are derived. Figure 17.109(b) shows the curves for injury to persons outdoors in the open and outdoors in a built-up area and Figure 17.109(c) to persons indoors in housing. Figure 17.109(d) shows the curves for all situations. There is one curve for injury by all modes to persons outdoors in the open and one for injury by all modes to persons outdoors in a built-up area or indoors in housing. The figures also gives curves for 50% probability of burdening injury. For persons subject to injury by glass fragments, however, the peak overpressures for 50% probability of fatality and burdening injury are taken as 11 and 1 psi, respectively.

17.40 Explosion Injury from Flying Glass

The shattering of window glass is an important blast damage effect, since flying glass can cause severe injury.

17.40.1 Experimental studies

There have been a number of experimental studies of the behaviour of, and injury by, flying glass and also studies of glass breakage following accidental explosions and of injury by flying glass in accidents and air raids.

Experiments on the breaking of glass windows by internal gas explosions have been described by Mainstone (1971 BRE CP 26/71) and M.R. Marshall, Harris and Moppett (1977).

The Eskimo series of trials, which involved the breaking of windows using large external charges of TNT, have been described by E.R. Fletcher, Richmond and Jones (1973) and E.R. Fletcher, Richmond and Richmond (1974). In Eskimo II the charge was 12.6 te and in Eskimo III 159 te.

Window breakage is among the damage effects of the explosion of 500 t TNT equivalent referred to by Fugelso, Weiner and Schiffman (1972).

There are also a number of accounts of the extent of window breakage following accidental explosions. Window breakage is one of the explosion effects analysed by C.S. Robinson (1944). Healy (1959) deals with window breakage in air raids.

The window breakage resulting from a large accidental explosion at Medina, San Antonio, Texas in 1963 has been described by Reed and co-workers (J.W. Reed *et al.*, 1968; J.W. Reed, 1980, 1992). The explosion involved 111 500 lb of high explosive, equivalent to 145 000 lb of TNT.

A review of window breakage is given by D.K. Pritchard (1981).

17.40.2 Flying glass models

A model for the behaviour of flying glass should cover the following features: (1) breaking pressure, (2) fragment characteristics, (3) velocity of fragments, (4) spatial density and (5) distance travelled by fragments. These features are now considered in turn.

17.40.3 Breaking pressure

The pressure at which windows break is generally quoted in terms of the peak side-on overpressure.

The force acting on the window is that of the peak reflected pressure. For a window directly facing the source of the explosion, the peak reflected pressure is some two times the peak side-on overpressure. For random orientation of windows J.W. Reed (1992) estimates an average reflection factor not of 2 but of 1.32.

The strength of window glass is very variable. It is not uncommon for an explosion to cause isolated window breakages at very considerable distances, and correspondingly low overpressures, while bangs from supersonic aircraft sometimes break windows at overpressures much less than those usually regarded as necessary to cause damage. Such instances, however, rarely cause injury.

Estimates of the peak side-on overpressure which causes window breakage have been given by a number of authors. Brasie and Simpson (1968) quote for the breaking pressure of glass windows a typical pressure of 1 kPa (0.145 psi). They also refer to breakage at low pressures of 0.2 kPa (0.029 psi) by sonic boom. Iverson (1968) gives the range of breaking pressures as 1–10 kPa (0.145–1.45 psi).

Some information on window breakage has already been given in Figure 17.92 and in Tables 17.43–17.44. Robinson's data show that for large explosions glass breakage can occur at great distances, of the order of 20 miles. The average glass breakage limit given in Table 17.44 is estimated by Brasie and Simpson (1968) to correspond to an overpressure of 0.006 psi, and they suggest that this is unrealistically low for estimation purposes.

Healy (1959) correlates window breakage in terms of the RB distance, and gives the following estimates:

RB distance	*Window breakage* (%)
5	90
10	50
20	5

These same estimates are given by Scilly and High (1986).

Glasstone (1962) gives the peak overpressure for window breakage as 0.5–1.0 psi (0.34–0.068 bar), as shown in Table 17.43, but without defining the proportion of windows broken.

Fugelso, Weiner and Schiffman (1972) give for the 500 t TNT equivalent explosion described above data on glass breakage also. These data have been analysed by Eisenberg, Lynch and Breeding (1975). The threshold or 1% level of glass breakage was 0.25 psi. They assume that the threshold level of structural damage corresponds to the 90% level for glass breakage and thus obtain the following data:

Glass breakage (%)	*Peak overpressure*	
	(psi)	(N/m^2)
1 (threshold)	0.25	1700
90	0.9	6200

They derive from these data a probit equation relating glass breakage to peak overpressure:

$$Y = -18.1 + 2.79 \ln p^o \qquad [17.40.1]$$

where p^o is the peak incident overpressure (Pa) and Y is the probit.

In the Eskimo trials described by E.R. Fletcher, Richmond and Jones (1973) and E.R. Fletcher, Richmond and Richmond (1974), the thickness of the panes tested ranged from 0.08 to 0.128 in. (2 to 3.25 mm) and from 0.203 to 0.264 in. (5.16 to 6.7 mm). All the windows were positioned directly facing the blast wave and the peak effective overpressure was taken as the peak reflected pressure, or twice the peak incident overpressure. Although the duration times in Eskimo II were significantly shorter than in Eskimo III, this did not significantly alter the breaking pressure, indicating that for such large explosions at least the breaking pressure is essentially independent of duration. Some results from these trials are as follows:

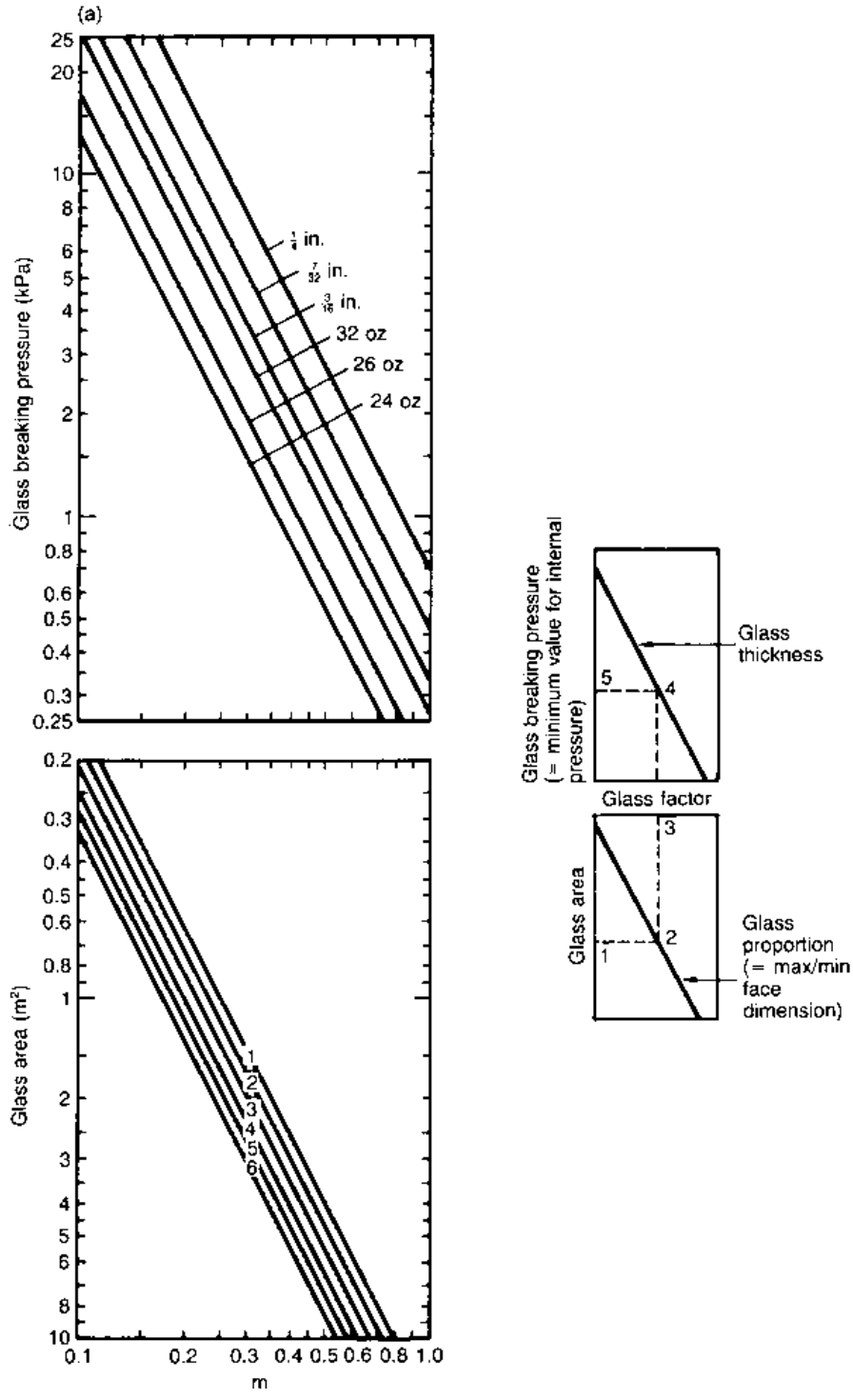


Figure 17.110 *Window breakage and flying glass from an internal gas explosion – breaking pressure of sheet glass panes (Mainstone, 1971): (a) sheet glass panes; and (b) plate glass panes (Courtesy of the Building Research Establishment)*

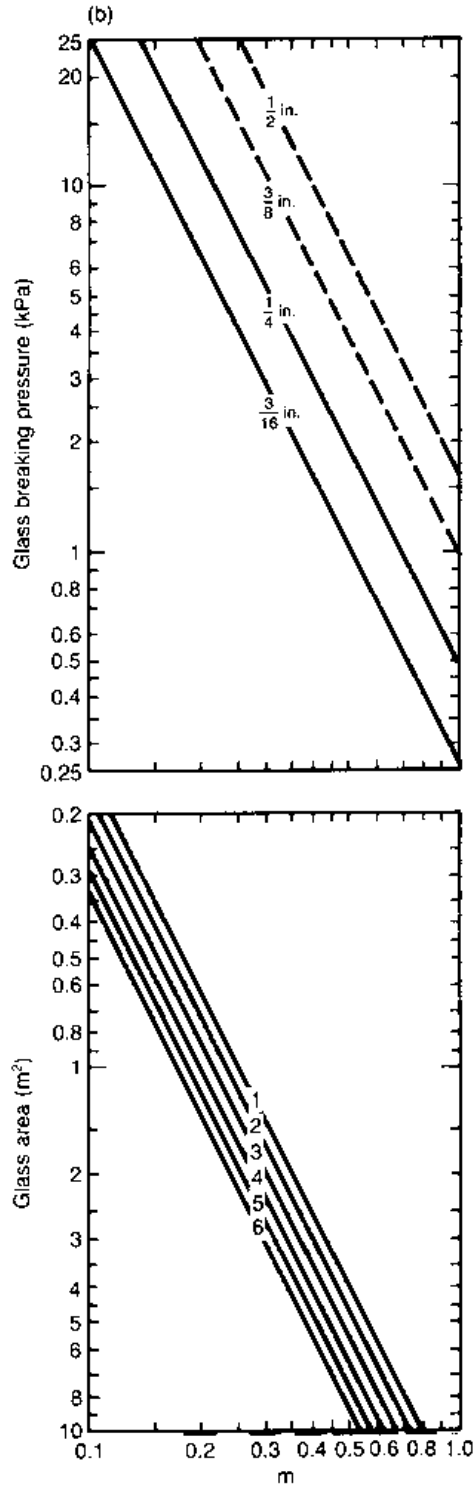


Figure 17.110 *continued*

Window size	*Breaking pressure*			
	Eskimo II		*Eskimo III*	
(m)	(Pa)	(psi)	(Pa)	(psi)
1.14 × 1.14	4830	0.70	4830	0.70
0.86 × 1.22	5930	0.86	5860	0.85

Window breakage in the Medina explosion has been analysed by Reed and co-workers (J.W. Reed *et al.*, 1968; J.W. Reed, 1980, 1992). The typical window is given by J.W. Reed (1992) as single-strength glass 2 ft × 2 ft × 2 mm thick. He gives a graph showing the probability of breaking versus the peak incident overpressure. Gilbert, Lees and Scilly (1994h) found that the relationship is a log-normal one, and give the following probit equation for breaking of a 'Reed' window:

$$Y = -4.77 + 1.09 \ln p_e^o \qquad [17.40.2]$$

where p_e^o is the peak effective overpressure (Pa) and Y is the probit. These authors also give the following relation for the determination of the peak effective overpressure for other windows for use in the above equation:

$$p_e^o = \left(\frac{A/0.372}{t/0.002}\right) p^o \qquad [17.40.3]$$

where A is the area of the pane (m^2), p^o is the peak incident overpressure (Pa), p_e^o is the peak effective overpressure for use in Equation 17.40.2 (Pa) and t is the thickness of the glass (m).

As already mentioned, experimental work on window breakage from internal gas explosions has been described by Mainstone (1971 BRE CP 26/71). Figure 17.110 shows the pressure for breakage for sheet glass panes of various thicknesses.

W.E. Baker *et al.* (1983) suggest that these data of Mainstone be treated as the quasi-static regime asymptote values.

Further experimental work on window breakage in internal gas explosions has been done by M.R. Marshall, Harris and Moppett (1977). Results from this work are given in Figure 17.111(a)–(d), showing breaking pressure as a function of glass thickness and window area.

These workers also investigated the behaviour of Georgian wired glass and glass treated with shatter resistant film, with the results shown in Figure 17.111.

Gilbert (1994) has analysed the results of Marshall, Harris and Moppett for plain glass windows as follows:

Window thickness (mm)	*Window size* (m × m)	*Pane area* (m^2)	*Breaking pressure Range* (kPa)	*Average* (kPa)	*Ratio of thickness to area* (1/m)
5	1.0 × 1.0	1.03	6.2–7.6	6.9	0.004 71
	1.0 × 0.5	0.515	8.3–11.7	10.0	0.018 9
	0.48 × 0.48	0.233	15.2–20.7	18.0	0.092 1
3	1.0 × 1.0	1.03	3.5–5.2	4.35	0.002 83
	1.0 × 0.5	0.515	6.9–8.3	7.6	0.011 3
	0.48 × 0.48	0.233	10.3–12.4	11.35	0.0553
4 (32 oz)	1.0 × 1.0	1.03	4.8	4.8	0.003 77

and derives from them the relation

$$p_{br}^* = 132\frac{t}{A} + 5.43 \qquad [17.40.4]$$

where p_{br}^* is the breaking pressure (kPa) and t is the thickness of the pane (m).

The overpressures necessary to cause window breakage have been reviewed in the *Second Report* of the ACMH (Harvey, 1979b). The report quotes for a typical dwelling house window of 24 oz glass of area 1 m^2 the work of Marshall, Harris and Moppett, indicating that a peak overpressure between about 0.03 and 0.05 bar is needed to break it. It concludes that for typical dwelling house windows the peak overpressures at which 50 and 90% window breakage is likely to occur are 0.016 and 0.038 bar, respectively, but emphasizes that the breaking pressure is a function of a large number of variables.

17.40.4 Fragment characteristics

I.G. Bowen *et al.* (1963b), cited by Hadjipavlou and Carr-Hill (1986), have given correlations for the mass and initial velocity of fragments from window breakage, though it is unclear under what conditions. They found that the mass distribution was log-normal and give the following probit equation:

$$Y = 5.97 + 0.86 \ln m \qquad [17.40.5]$$

where m is the mass of the fragment (g) and Y is the probit. The median value of the mass ($Y = 5$) is thus 0.324 g.

E.R. Fletcher, Richmond and Richmond (1974) characterize glass fragments in terms of the mean mass m_{50} and mean frontal area A_{50}. Their expression for the latter, in the form given by E.R. Fletcher, Richmond and Yelverton (1980), is

$$\ln A_{50}^* = 4.2643 - (12.5 + 0.003\,43 p_e^{o*2})^{\frac{1}{2}} \qquad [17.40.6]$$

where A_{50}^* is the mean frontal area (cm^2) and p_e^{o*} the peak effective overpressure (kPa).

The mean mass m_{50} may be then obtained as

$$m_{50} = A_{50}\rho_{gl}t \qquad [17.40.7]$$

where A_{50} is the mean frontal area of the fragment (m^2), m_{50} is the mean mass of the fragment (kg), t is the thickness of the fragment (m) and ρ_{gl} is the density of glass (kg/m^3).

This mean frontal area is not necessarily the mean presented area (MPA) on impact. This latter depends on the behaviour of the fragment during flight. Consider a fragment of rectangular cross-section and uniform thickness with a length : width ratio of 2 : 1. If the length of the long side is l and the thickness is t, the width is $l/2$ and the area A_{50} is $l^2/2$. For a fragment approaching a target square on there are three possible MPAs: $l^2/2$, lt and $lt/2$. Taking the second of these, or the intermediate case, the MPA is then

$$A_{mp} = (2A_{50})^{\frac{1}{2}}t \qquad [17.40.8]$$

where A_{mp} is the MPA of the fragment on impact (m^2) l is the length of the fragment (m) and t is the thickness of the fragment (m).

A further treatment of fragment characteristics is given in Section 17.40.6.

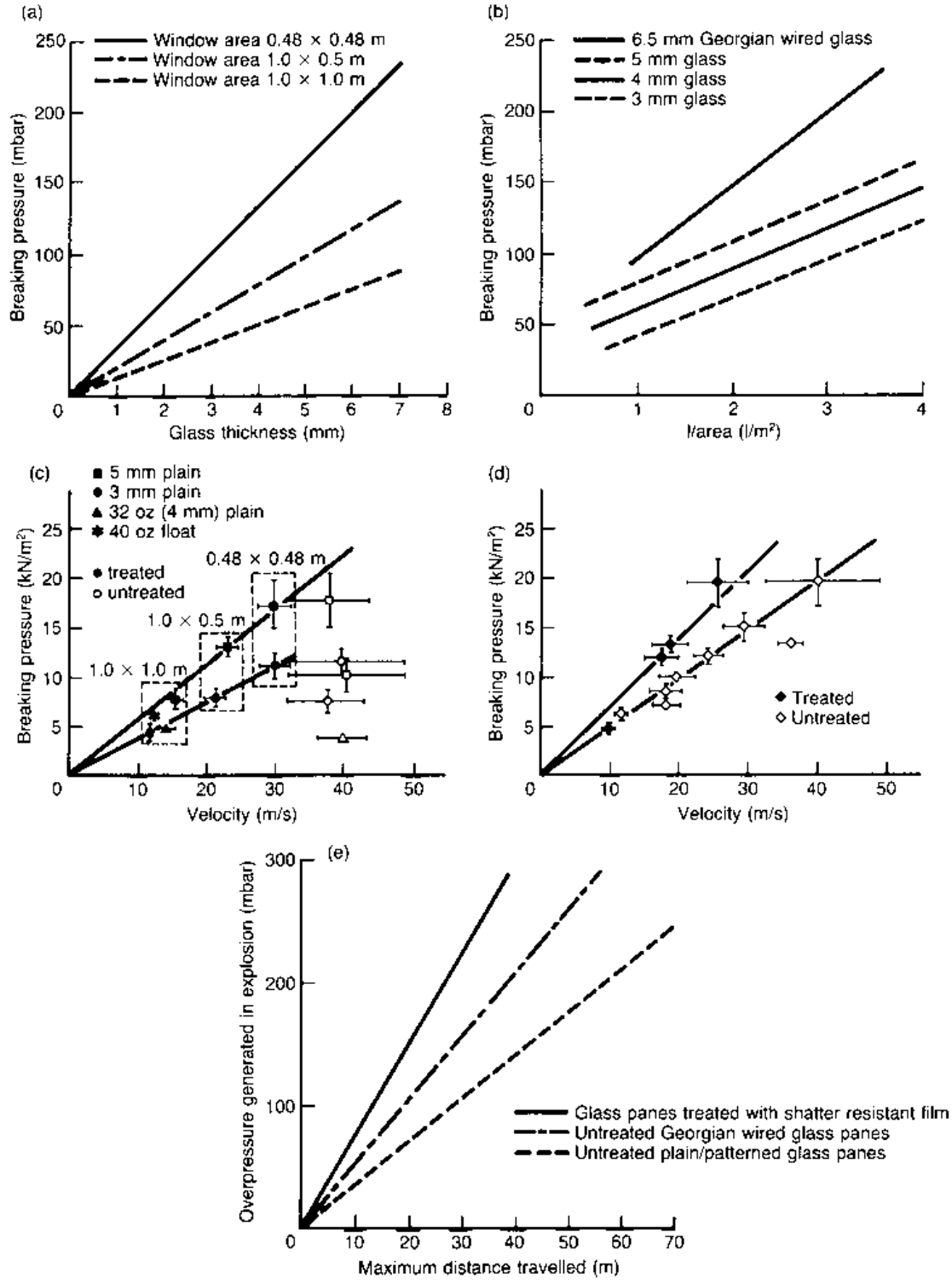


Figure 17.111 *Window breakage and flying glass – breaking pressure of windows and characteristics of flying glass (M.R. Marshall, Harris and Moppett, 1977): (a) breaking pressure as function of glass thickness; (b) breaking pressure as function of window area; (c) velocity of glass fragments, plain glass; (d) velocity of glass fragments, Georgian wired glass; (e) distance travelled by glass fragments (Courtesy of the Institution of Chemical Engineers)*

17.40.5 Velocity of fragments

A treatment of the velocity of glass fragments is given by Glasstone (1962). He gives a correlation in terms of the geometric mean velocity V'_{50}, or antilogarithm of the mean of the logarithms of the velocities. He uses a scaled geometric mean velocity $\bar{V}'_{50}$, which allows for the thickness of the glass and which is defined as

$$\bar{V}'_{50} = \frac{V'_{50}}{0.83 + 0.019(t' - 0.03)^{-0.93}} \qquad [17.40.9]$$

where t' is the pane thickness (in.), V'_{50} is the geometric mean velocity (ft/s) and $\bar{V}'_{50}$ is the scaled geometric mean velocity (ft/s). The correlation relates the scaled geometric mean velocity to the peak effective overpressure applicable to conventional explosions of 15–500 t. Glasstone states that the correlation is based on experiments with various types of glass ranging from 0.25 in. thick plate glass, through various standard thicknesses of single- and double-strength glass, to non-standard glass panes 0.064 in. thick. This correlation may be represented as

$$\ln \bar{V}'_{50} = 3.746 + 0.546 \ln p'^{o}_{e} \qquad [17.40.10]$$

where p'^{o}_{e} is the peak effective overpressure (psi).

In the work described earlier, I.G. Bowen *et al.* (1963b) found that the velocities of fragments from window breakage had a log-normal distribution, and gave the probit relation

$$Y = -11.7 + 4.41 \ln V \qquad [17.40.11]$$

where V is the velocity of the fragment (m/s). The median value of the fragment mass was 0.324 g and the median value of the velocity from Equation 17.40.11 is 44 m/s.

A correlation of the initial velocity in the Eskimo trials is given by E.R. Fletcher, Richmond and Richmond (1974). Their expressions for the latter, in the form given by E.R. Fletcher, Richmond and Yelverton (1980), are as follows. A scaled velocity $\bar{V}_{50}$ is defined as

$$\bar{V}_{50} = \left(\frac{V_{50}}{0.833 + 0.04465(t^* - 0.0762)^{-0.928}} \right) \qquad [17.40.12]$$

where t^* is the thickness of the pane (cm), V_{50} is the geometric mean velocity (m/s) and $\bar{V}_{50}$ is the scaled geometric mean velocity (m/s). The correlation is

$$\ln \bar{V}_{50} = 1.5241 + 0.547 \ln p^{o}_{e}* \qquad [17.40.13]$$

where $p^{o}_{e}*$ is the peak effective pressure (kPa).

E.R. Fletcher, Richmond and Yelverton (1980) also give data on average impact velocity of fragments from which the following relation may be inferred:

$$\ln V = 1.5241 + 0.55 \ln p^{o}_{e}* \qquad [17.40.14]$$

where $p^{o}_{e}*$ is the peak effective overpressure (kPa) and V is the average velocity (m/s).

For an internal gas explosion the velocity of fragments from a breaking window is given by M.R. Marshall, Harris and Moppett (1977) in the work described earlier, as shown in Figure 17.111(c). The velocity concerned is the average velocity over the first 6 m of travel. The mean values of the velocities in Figure 17.111(c) are in the range 35–40 m/s.

These data have been analysed by Gilbert, Lees and Scilly (1994h). The data for untreated unwired windows show wide scatter, but from those for wired glass there appears to be a factor of about 1.38 between the velocities from untreated and treated windows. Applying this same factor to the velocities from treated, unwired windows gives for untreated, unwired windows

$$V = 11.57 \frac{p^*_{br}}{0.001t} \qquad [17.40.15]$$

where p^*_{br} is the breaking pressure (kPa), t is the thickness of the glass (m) and V is the average velocity of the fragments (m/s).

17.40.6 Velocity of fragments: method of Baker *et al.*

W.E. Baker *et al.* (1983) give the following treatment for the velocity of fragments from breaking windows based on the work of E.R. Fletcher, Richmond and Jones (1973, 1976). An effective peak overpressure P_e is defined, which for windows side-on or back-on to the blast wave is equivalent to the peak incident overpressure P_s and for those face-on to the peak reflected overpressure P_r. The latter may be obtained as follows:

$$\bar{P}_r = 2\bar{P}_s + \frac{(\gamma+1)\bar{P}_s^2}{(\gamma-1)\bar{P}_s + 2\gamma} \qquad \bar{P}_s \leq 3.5 \qquad [17.40.16]$$

with

$$\bar{P}_s = P_s/P_o \qquad [17.40.17]$$

$$\bar{P}_r = P_r/P_o \qquad [17.40.18]$$

where P_o is atmospheric pressure (Pa), P_e is the peak effective overpressure (Pa), P_r is the peak reflected overpressure (Pa), $\bar{P}_r$ is the dimensionless peak reflected overpressure, P_s is the peak side-on overpressure (Pa), and $\bar{P}_s$ is the dimensionless peak side-on overpressure. For $\bar{P}_s > 3.5$ the authors give an alternative equation (their Equation 3.5).

On the assumption that all the fragments are square, the mass of a fragment is

$$M = y^2 t \rho_{gl} \qquad [17.40.19]$$

where M is the mass of the fragment (kg), t is the thickness of the glass (m), y is the length of the square edge (m) and ρ_{gl} is the density of glass (kg/m^3). The density of glass may be taken as 2471 kg/m^3.

The geometric mean frontal area A'_{50} of the fragments is given by the equation

$$A'_{50} = 6.45 \times 10^{-4} \exp\{2.4 - [12.5 + (5.86 \times 10^{-5} P_e)^2]^{\frac{1}{2}}\}$$

$$0 < P_e < 96500 \qquad [17.40.20]$$

where A'_{50} is the geometric mean frontal area (m^2).

If all the fragments travel with the flat face forward, the presented area A of the fragments is

$$A = A'_{50} \qquad [17.40.21]$$

while if all fragments travel edge forward

$$A = tA'^{\frac{1}{2}}_{50} \qquad [17.40.22]$$

where A is the presented area of the fragment (m^2).

The ratio A/M for these two cases is, respectively

$$\frac{A}{M} = \frac{1}{t\rho_{gl}} \qquad [17.40.23]$$

and

$$\frac{A}{M} = \frac{1}{\rho_{gl}A'^{\frac{1}{2}}_{50}} \qquad [17.40.24]$$

The lower value of A/M given by these two alternative equations is selected.

The geometric mean velocity V_{50} of the fragments is given in SI units by the equation

$$V_{50} = [0.2539 + (1.86 \times 10^{-4})$$

$$(t - 7.62 \times 10^{-4})^{-0.928}](0.3443P_e^{0.547})$$

$$690 < P_e < 689\,000;\ t \geq 7.62 \times 10^{-4} \qquad [17.40.25]$$

where V_{50} is the geometric mean velocity (m/s).

17.40.7 Spatial density of fragments

A correlation for the spatial density of glass fragments from window breakage based on the Eskimo trials is given by E.R. Fletcher, Richmond and Richmond (1974). Their expression for the latter, in the form given by E.R. Fletcher, Richmond and Yelverton (1980), is as follows. A scaled spatial density $\bar{\rho}'_{sd}$ is defined as

$$\bar{\rho}'_{sd} = \frac{\rho_{sd}}{4.91\ \exp(-5.0121) + 22.28} \qquad [17.40.26]$$

and gives the correlation

$$\ln \bar{\rho}'_{sd} = 3.1037 + 0.058\,57p^o_e* \qquad [17.40.27]$$

where p^o_e* is the peak effective overpressure (kPa) and ρ_{sd} is the spatial density (fragments/m^2).

17.40.8 Range of fragments

For an internal gas explosion the distance travelled by fragments from a breaking window is given by M.R. Marshall, Harris and Moppett (1977) in the work already described, as shown in Figure 17.111(e).

17.40.9 Injury relations

Glasstone (1962) gives the data on injury effects caused by glass fragments of different impact velocities shown in Table 17.58.

Methods for the estimation of serious injury from flying glass have been given in the vulnerability model by Eisenberg, Lynch and Breeding (1975) and by W.E. Baker *et al.* (1983). These are described in Sections 17.40.10 and 17.40.11, respectively.

Hadjipavlou and Carr-Hill (1986) have analysed data from animal experiments and have proposed the following probit equations for laceration and for penetration:

$$Y = -12.23 + 0.83 \ln mV' \qquad \text{Laceration} \qquad [17.40.28]$$

$$Y = -8.35 + 0.61 \ln mV' \qquad \text{Penetration} \qquad [17.40.29]$$

where m is the mass of the fragment (g) and V' is its velocity (ft/s).

Table 17.58 *Some data on injury effects caused by glass fragments (after Glasstone, 1962)*

A Penetration of abdomen wall: impact velocity (ft/s)

Mass of glass fragment (g)	*Probability of penetration* (%)		
	1	*50*	*99*
0.1	235	410	730
0.5	160	275	485
1.0	140	245	430
10.0	115	180	355

B Injury from penetrating 10 g fragments

Effect	*Impact velocity* (ft/s)
Skin laceration:	
Threshold	50
Serious wounds:	
Threshold	100
50%	180
Nearly 100%	300

A method of determining the probability of fatality for a person standing behind a window is given in the *Green Book* and is described in Section 17.40.12.

Gilbert, Lees and Scilly (1994f) have given a model for fatal and non-fatal injury by any potentially penetrating fragment. This is applicable to flying glass, as described in Section 17.42.

17.40.10 Injury relations: vulnerability model method

The treatment of injury by flying glass in the vulnerability model described by Eisenberg, Lynch and Breeding is as follows. The impact velocity of a missile V_i is related to the impulse J by the equation

$$MV_i = C_D AJ \qquad [17.40.30]$$

where A is the presented area of the missile (m^2), C_D is the drag coefficient, J is the impulse (Pa s), M is the mass of the missile (kg), and V_i is the impact velocity (m/s). The value of the drag coefficient C_D is taken as unity.

For injury from flying glass they consider a 10 g fragment and quote the data given in the second and third columns of the following table, which is derived from information given by the Department of the Army (1969):

Injury	*Peak overpressure* (psi)	*Impact velocity* (m/s)	*Impulse* (psi ms)	*Impulse* (Pa s)
Skin laceration				
Threshold	1–2	15	74.2	512
Serious wound				
Threshold	2–3	30	148.4	1024
50%	4–5	55	272.1	1877
Near 100%	7–8	90	445.3	3071

They derive from this the impulse values given in columns four and five of the above table and hence a probit equation relating serious injury from missiles, particularly glass, to impulse:

$$Y = -27.1 + 4.26 \ln J \qquad [17.40.31]$$

It is assumed in the application of Equation 17.40.31 that all personnel not inside buildings who are in the region traversed by a blast wave of sufficient strength suffer injury from missiles. The density of flying fragments and the target area presented by people are not factors affecting the probability of injury in this analysis. Thus the equation overestimates by a considerable factor the extent of injury by flying fragments. This particular probit equation, therefore, should be regarded as representing an upper bound.

17.40.11 Injury relations: method of Baker *et al.*

The treatment for injury by glass fragments given by W.E. Baker *et al.* (1983) is based on the work of Sperrazza and Kokinakis (1967, 1968), but is essentially similar. For the fragment velocity they use the correlations obtained by Fletcher and co-workers and described in Section 17.40.6.

Sperrazzo and Kokinakis carried out experiments on the perforation of the skin of animals. Baker *et al.* give a straight-line graph of the results of this and other work, including that quoted by Glasstone, to which they fit with the relation

$$V_{50} = 22.03 + 1247.1\frac{A}{M} \qquad \frac{A}{M} < 0.09; M \leq 0.015 \qquad [17.40.32]$$

where A is the presented area of the fragment (m^2), M is its mass (kg) and V_{50} is the velocity for 50% probability of perforation (m/s).

It is assumed by Sperrazzo and Kokinakis that if a fragment perforates the skin, its residual velocity will be sufficient to do severe injury. Baker *et al.* suggest that this assumption incorporates a margin of safety.

17.40.12 Injury relations: *Green Book*–method

The *Green Book* gives a probit equation for fatality due to impact of glass fragments on the head of a person standing 1.75 m behind the window pane. The equation is

$$Y = 2.67 + \ln\left(\frac{f_{dl}P^o}{P_{st}}\right) \qquad [17.40.33]$$

where f_{dl} is the dynamic load factor, P^o is the peak incident overpressure (Pa) and P_{st} is the static strength of the pane (Pa).

The basis of this equation is tests in which the peak reflected pressure was twice the dynamic failure load P_{df} of the panes and in which the probability of fracture of the skull was estimated as 94%. Then for these conditions $P_{df} = P_{st}/f_{dl}$ and $P^o = 2P_{st}/f_{dl}$. Hence $P^o/(P_{st}/f_{dl}) = 2$. It was assumed that for 1% lethality $P^o/(P_{st}/f_{dl}) = 1$. The probit equation is derived from these two values.

The static strength of the pane is obtained from the relations

$$f_t = \frac{2 \times 10^6}{A^{0.18}d^{0.7}} \qquad [17.40.34]$$

and

$$f_t = 0.225P_{st}\frac{a^2}{d^2} \qquad [17.40.35]$$

where a is the smaller of the two dimensions of the pane (m), A is the area of the pane (m^2), d is the thickness of the pane (m) and f_t is the tensile strength of the pane (Pa).

Thus a window $1.5 \times 1.0 \times 0.005$ m has a tensile strength $f_t = 75.9 \times 10^6$ Pa and a static strength $P_{st} = 8.43 \times 10^3$ Pa.

The dynamic load factor f_{dl} is a function of the ratio t_d/T of the duration time t_d to the natural period of vibration T. It has a value less than 1 for a short duration ($t_d \ll T$) and of 2 for a long duration ($t_d \gg T$).

17.40.13 Flying glass: model of Gilbert, Lees and Scilly

Gilbert, Lees and Scilly (1994f) have given a model for the probability of incurring various degrees of injury due to impact of a potentially penetrating fragment. This model is described in Section 17.42. It is applicable to injury by fragments from window breakage.

In another paper, Gilbert, Lees and Scilly (1994h) have used this model in combination with some of the relations given above to provide an integrated treatment for the estimation of injury from flying glass. The model is applicable to the explosion of a condensed phase explosive external to the building.

The approach used in this integrated model is as follows. The characteristics of the window typical of the scenario considered are determined. Following Reed, the average peak reflected overpressure is taken as 1.32 times the peak incident overpressure. From Equation 17.40.3 the peak incident overpressure to produce an equivalent load on a 'Reed' window is estimated. Using Equation 17.40.2, the probability of window breakage is estimated. Given that the window is broken, Equations 17.40.6, 17.40.7, 17.40.14 and 17.40.27 are used to obtain the mean frontal area, mass, velocity and spatial density of the fragments. Then using the fragment injury model of the authors, the probability of fatal and non-fatal injury is determined.

17.40.14 Flying glass hazard

The question of injury from flying glass is considered in the *Second Report* of the ACMH (Harvey, 1979b). The report is particularly concerned with the risks from a vapour cloud explosion.

In general, much of the concern about possible injury from flying glass relates to injury to people indoors. The shattering of glass as a result of an explosion has occurred at distances up to 20 miles. In such cases, however, the energy of the fragments is very low. The evidence appears to indicate that there are surprisingly few injuries to people from glass fragments even in buildings where most of the windows have been shattered by blast.

The report describes first the historical record. A large number of windows were broken in the vapour cloud explosions both at Flixborough and at Beek. At Beek there were 2508 cases of damage outside the factory and these were almost entirely glass breakage (Case History A75). One person was injured by glass.

The report refers to the experimental work M.R. Marshall, Harris and Moppett (1977) on the breakage of glass windows by explosions inside buildings. In this work the peak overpressure was in the range 0.03–0.25 bar. The fragment velocities measured were high, being of the order of 40 m/s, and varied relatively little. The report argues, however, that these results are not applicable to the very different conditions of explosions outside buildings.

This latter situation is then considered. It is estimated in the report that the overpressures required to effect 50 and 90% breakage of windows are about 0.016 and 0.038 bar, respectively. A breakage of 50% implies a non-breakage of 50% of the windows, which suggests that the fragment velocity is likely to be low.

The report quotes experimental work in the USA in which windows 1/8 in. and 1/4 in. thick were mounted at various distances from large masses of TNT so that overpressures of 0.3 psi (0.02 bar), 0.5 psi (0.035 bar) and 0.6 psi (0.04 bar) with a duration time of 250 ms were applied to them, and fragment masses and velocities were determined. Separate experiments were conducted to find the probability that such fragments would penetrate bare skin, or clothed skin, or 1 cm of soft tissue. Only 1 fragment, out of 90, from the thicker windows broken at the highest pressure was found to have a 10% probability of penetrating 1 cm. No other fragment had even 1% probability of this degree of penetration.

It is concluded in the report that there is ample justification for regarding as negligible the risk of injury from flying fragments of window glass for an explosion which gives a peak overpressure outside the building of 0.6 psi (0.04 bar) or less.

17.41 Explosion Injury from Penetrating Fragments

One of the principal modes of injury from an explosion is wounding by penetrating fragments. In this section the information available on the wounding and incapacitating power of fragments is reviewed and several criteria and models for injury by a penetrating fragment are given. A further model for such injury by Gilbert, Lees and Scilly (1994f) is described in the next section.

This problem is of particular interest to the military, and much of the data are from military sources. These include the *Textbook* and the work of Gurney (1944), Dunn and Sterne (1952) and Beyer (1962). The work of the Stockholm International Peace Research Institute (SIPRI) (1978) is also relevant.

17.41.1 Definition of injury

The degree of injury of prime interest to the military is incapacitation, and much of the information available on injury by penetrating fragments relates to this. An account of the incapacitating power of weapons has been given in a review by SIPRI (1978).

This review emphasizes that the interpretation of incapacitating power is not straightforward. The military interest is in the ability of a projectile to cause rapid incapacitation, in other words its stopping power. Stopping power, however, is not synonymous with wounding power.

Work in the USA during and after the Second World War showed that immediate incapacitation is obtained only by severe injury to parts of the spinal column or brain. It is harder to achieve than fatal or severe injury, which results from injury to major organs or blood vessels.

Dunn and Sterne (1952) carried out experiments in which projectiles were fired at goats. They found that the probability of incapacitation was much less than for ultimate fatal or severe injury. SIPRI summarize their work to the effect that even for the most effective projectile the probability of fatal or severe injury is three to four times greater than the probability of immediate incapacitation.

The main sources of data on the injuring power of fragments refer to incapacitation, but in order to be able to utilize them it is necessary to be able to interpret incapacitation and to relate it to fatal and severe injury.

The meaning of incapacitation is discussed in the *Textbook*. It states:

> Despite the shortcomings of the available information, it is safe to conclude, from the data that have been summarized here, that any penetrating splinter wounds of the head, neck and trunk are highly dangerous, and that almost any wound may be regarded as incapacitating (which for convenience may be defined as a wound necessitating medical attention), provided that the missile concerned gets through the skin into the underlying tissues. In the case of limbs, single splinter wounds are not as dangerous, and the relative number of hits by small splinters which would prove incapacitating is clearly smaller.

The *Textbook* then discusses wounds by small splinters, treating separately the head and neck, the thorax and abdomen, and the limbs. The criteria used for incapacitating wounds are:

Head	Perforation of the skull
Thorax and abdomen	Perforation of trunk
Limbs	Penetration to half-depth and hitting central supporting bone

The *Textbook* states that a rough estimate of the proportion of the total projected area of the body which represents the vital organs, where a battle injury due to a small missile would result in almost certain death, is roughly 10–15%.

The most vulnerable parts of the body are the head and neck and the thorax and abdomen. These account for some 39% of the projected area of the body.

17.41.2 Causative factor

There are two basic types of relation which are used for the damaging, or injuring, power of a fragment, or projectile. One is the relation for kinetic energy

$$E = mu^2/2 \qquad [17.41.1]$$

where E is the kinetic energy (J), m is the mass of the fragment (kg) and u is the velocity (m/s). This equation also may be written in the alternative form

$$um^{0.5} = \text{Constant} \qquad [17.41.2]$$

The other type of relation, which is widely used in correlating penetration by a projectile, is

$$um^c = \text{Constant} \qquad [17.41.3]$$

where c is an index. Equation 17.41.3 is equivalent to Equation 17.41.2 for $c = 0.5$.

It is now recognized that the mean presented area (MPA) of the fragment is also relevant. This is discussed in Section 17.42.

17.41.3 Incapacitation criteria

At the turn of the last century the German army adopted a projectile kinetic energy of 78 J (58 ft lb) as incapacitating to military personnel. This is also the value which has traditionally been used in Britain and the USA.

Other criterion values quoted by SIPRI are the French, Swiss and Russian values of 39, 62 and 235 J, respectively.

According to Beyer (1962) this type of criterion has proved a better indicator of incapacitating power than measures such as penetration into solid objects such as pine boards.

The 78 J criterion has been discussed by Gurney (1944), who states that it is valid for fragments in the range 50 mg to 30 g.

More sophisticated criteria have since been developed for weapons design, based on actual casualty data and taking into account the different areas of the body hit.

A computer code for the estimation of incapacitation by bullets, COMPUTER MAN, has been developed by the US Army. In this code the human body is divided into small sections ($5 \times 5 \times 25$ mm) with the tissue type within the each section specified. The model is then utilized in conjunction with information on the impact points of bullets, their ballistic properties, etc., to obtain a ranking on a relative incapacitation index (RII).

A commercial computer code, WBD2, is also available, developed by Timberwolf Consulting Services (1991), which embodies a wound ballistics simulation model.

An interpretation of the 78 J incapacitation criterion has been given by Gilbert, Lees and Scilly (1994f), who conclude that it in terms of the *Textbook* incapacitation model, described below, the criterion corresponds approximately to a 90% probability of incapacitation.

17.41.4 *Textbook* model

A model for the incapacitating power of a penetrating fragment is given in the *Textbook*. The basic relation used is the penetration equation

$$P = kV^b m^c \qquad [17.41.4]$$

where m is the mass of the fragment (mg), P is the penetration (ft) and V is the velocity (ft/s), k is a constant and b and c are indices. It follows from Equation 17.41.4 that for a given incapacitating power

$$V^b m^c = \text{Constant} \qquad [17.41.5]$$

or

$$v = V(m/m_r)^{c/b} \qquad [17.41.6]$$

where m_r is the mass of a reference fragment (mg) and v is the equivalent velocity (ft/s). The values given for b and c are 1 and 0.4, respectively.

A standard fragment is defined for which the value of m_r is 52 mg. The *Textbook* gives probit relations for incapacitation by 52 mg fragments of different shape. The relations are formulated in terms of velocity as the causative factor. The probability of incapacitation by a fragment of given mass and velocity is then obtained by determining the equivalent velocity from Equation 17.41.6 and using this value in the probit relations.

It may be noted that this standard fragment size of 52 mg is small but that a large proportion of the fragments are of this size or below. However, some doubt must attach to extrapolation of the correlation to much larger fragment sizes.

This model applies to a soldier wearing the full complement of land service clothing and equipment, including a helmet.

The *Textbook* model has been cast in convenient form by Gilbert, Lees and Scilly (1994f). For a 52 mg cuboid fragment the probit relation in terms of the velocity u is

$$Y = -8.25 + 1.96 \ln u \qquad [17.41.7]$$

where u is the velocity of the fragment (m/s).

As just indicated, Equation 17.41.7 is specific to a 52 mg fragment. Generalizing for other fragments, by using the causative factor $um^{0.4}$ used in the *Textbook*, these authors obtain

$$Y = -0.51 + 1.96 \ln(um^{0.4}) \qquad [17.41.8]$$

where m is the mass of the fragment (kg).

Gilbert, Lees and Scilly have also adapted the *Textbook* model to the estimation of fatal and serious injuries (K + SI). This is based on equating a 10% probability of incapacitation to a 30% probability of fatal or serious injury, whilst retaining the slope of the probit equation. The equation obtained is

$$Y = 0.24 + 1.96 \ln(um^{0.4}) \qquad [17.41.9]$$

17.42 Explosion Injury from Penetrating Fragments: Model of Gilbert, Lees and Scilly

A model for injury from fragments and missiles generated by an explosion has been given by Gilbert, Lees and Scilly (1994f,g). The model is applicable to the assessment of injury caused by impact of any missile which has the potential to penetrate the skin; it is not intended for the assessment of impact by blunt objects. It was developed primarily with reference to the hazard of fragments from the casing of munitions.

17.42.1 Classification of injury

The injury classification used is:

- K Injury which is fatal, either immediately or in hospital
- S Injury which is serious, involving perforation of the skin, and which necessitates medical attention, implying hospitalization
- M Injury which is generally not serious, involving perforation of skin, but which deserves medical attention
- T Injury which is trivial, possibly penetrating the skin but not perforating it, or no injury at all

A serious injury is defined more specifically as one involving the following:

Head and neck	Perforation of the skull
Thorax	Penetration of the 'vulnerable area'
Abdomen	Penetration of the 'vulnerable area'
Limbs	Penetration of the 'vulnerable area'

The abdomen is taken to mean the abdomen proper and that part of the thorax which is not protected by bone, whilst the thorax is taken as that part of the chest which is so protected.

17.42.2 Probability of injury

The following probabilities are defined:

$P(\mathrm{H})$	Probability of hit by fragment
$P(\mathrm{H}_i)$	Probability of hit by fragment in body region i
$P(\mathrm{K})$	Probability of fatal injury
$P(\mathrm{K}_i)$	Probability of fatal injury in body region i
$P(\mathrm{S})$	Probability of serious injury
$P(\mathrm{S}_i)$	Probability of serious injury in body region i
$P(\mathrm{P}_{\mathrm{vul},i})$	Probability of penetration of vulnerable area of body region i, equal to probability of fatal or serious injury in that region
$P(\mathrm{P}_{\mathrm{skin}})$	Probability of perforation of skin
$P(\mathrm{P}_{\mathrm{skull}})$	Probability of perforation of skull
$P(\mathrm{P}_{\mathrm{thor}})$	Probability of penetration of vulnerable area of thorax
$P(\mathrm{P}_{\mathrm{abd}})$	Probability of penetration of vulnerable area of abdomen
$P(\mathrm{P}_{\mathrm{limb}})$	Probability of penetration of vulnerable area of limb

Use is also made of the subscripts lwlimb and uplimb to denote lower and upper limbs, respectively. The last four probabilities are conditional probabilities, as defined below.

It is assumed that if the body is hit at all by a fragment, the effect is classified using one of the four categories. The trivial injury category covers the cases where the injury is trivial or where no injury is sustained, so that the sum of the probabilities of injury in these four categories is always unity.

The probability of a hit on body region i is

$$P(\mathrm{H}_i) = A_i/A \qquad [17.42.1]$$

where A is the total MPA of the body and A_i is the MPA attributable to region i.

The probability of perforation of the skin is a function of fragment mass, projected area and velocity. It is assumed that perforation of the skin by a fragment will result in either fatality, serious injury or medium injury (K, S or M).

The probability of penetration to a vulnerable area in a particular region i of the body is

$$P(\mathrm{P}_{\mathrm{vul,\,i}}) = P(\mathrm{P}_{\mathrm{vul,\,i}}|P_{\mathrm{skin}})P(\mathrm{P}_{\mathrm{skin}}) \qquad [17.42.2]$$

Specifically, for each region considered,

$$P(\mathrm{P}_{\mathrm{vul,\,i}}\,|\mathrm{P}_{\mathrm{skin}}) = P(\mathrm{P}_{\mathrm{skull}}) \qquad \text{Head and neck} \qquad [17.42.3]$$

$$= P(\mathrm{P}_{\mathrm{thor}}) \qquad \text{Thorax} \qquad [17.42.4]$$

$$= P(\mathrm{P}_{\mathrm{abd}}) \qquad \text{Abdomen} \qquad [17.42.5]$$

$$= P(\mathrm{P}_{\mathrm{limb}}) \qquad \text{Limb} \qquad [17.42.6]$$

Then for the head and neck

$$P(\mathrm{P}_{\mathrm{vul,\,i}}) = P(\mathrm{P}_{\mathrm{skull}})P(\mathrm{P}_{\mathrm{skin}}) \qquad [17.42.7]$$

for the thorax

$$P(\mathrm{P}_{\mathrm{vul,\,i}}) = P(1P_{\mathrm{thor}})P(\mathrm{P}_{\mathrm{skin}}) \qquad [17.42.8]$$

for the abdomen

$$P(\mathrm{P}_{\mathrm{vul,\,i}}) = P(\mathrm{P}_{\mathrm{abd}}P(\mathrm{P}_{\mathrm{skin}}) \qquad [17.42.9]$$

and for the limbs

$$P(\mathrm{P}_{\mathrm{vul,\,i}}) = P(\mathrm{P}_{\mathrm{limb}})P(\mathrm{P}_{\mathrm{skin}}) \qquad [17.42.10]$$

In this model, the probability of fatal or serious injury (K or S) in body region i is defined by $P(\mathrm{P}_{\mathrm{vul},i})$. The probability of fatal injury is

$$P(\mathrm{K}_i) = P(\mathrm{K}_i|\mathrm{P}_{\mathrm{vul,\,i}})P(_{\mathrm{vul,\,i}}) \qquad [17.42.11]$$

The probability of serious injury in body region i is then

$$P(\mathrm{S}_i) = P(\mathrm{P}_{\mathrm{vul,\,i}}) - P(\mathrm{K}_i) \qquad [17.42.12]$$

The overall probability of fatal injury is

$$P(\mathrm{K}) = \sum P(\mathrm{K}_i) \qquad [17.42.13]$$

and that of serious injury is

$$P(\mathrm{S}) = \sum P(\mathrm{S}_i) \qquad [17.42.14]$$

The overall probability of trivial or no injury is

$$P(\mathrm{T}) = 1 - P(\mathrm{P}_{\mathrm{skin}}) \qquad [17.42.15]$$

and that of medium injury is simply the residue

$$P(\mathrm{M}) = 1 - [P(\mathrm{K}) + P(\mathrm{S}) + P(\mathrm{T})] \qquad [17.42.16]$$

The probabilities which need to be estimated for this model are therefore for the perforation of the skin $P(\mathrm{P}_{\mathrm{skin}})$ and the following probabilities for each body region i: $P(\mathrm{P}_{\mathrm{vul,\,i}}|\mathrm{P}_{\mathrm{skin}})$ and $P(\mathrm{K}|\mathrm{P}_{\mathrm{vul,\,i}})$

17.42.3 Causative factor

Traditionally the criterion for military incapacitation has been expressed in terms of a kinetic energy. Later it became recognized that the presented area of the fragment was also relevant.

It has become usual to work, therefore, in terms of the following causative factor X:

$$X = mu^2/A \qquad [17.42.17]$$

where A is the projected area of the fragment (m^2), m is its mass (kg), u is its velocity (m/s) and X is the causative factor ($\mathrm{J/m}^2$).

17.42.4 Perforation of skin

A distinction is made between skin penetration, or epidermis perforation, and skin perforation, or full-depth perforation.

The problem of skin perforation is relatively complex. In a review of work on this topic Di Maio (1981) makes a distinction between experiments carried out on sample of skin with, and without, subcutaneous tissue attached. Skin seems to be more resistant to fragment penetration when it is *in situ*, with underlying muscle and fat still attached.

Some information on the properties of the skin is provided by Mehta and Wong (1967). Experimental work on skin perforation using unattached skin has been described by Grundfest *et al.* (1945) and Sperrazza and Kokinakis (1968). Accounts of experiments on attached skin have been given by Journée (1907), Mattoo, Wani and Askegar (1974) and Di Maio *et al.* (1982). A review of work on penetrating trauma has been given by Neades and Rudolph (1983) as part of an attempt to

improve on the widely used criterion for incapacitation of 78 J.

The model adopted by Gilbert, Lees and Scilly is that of J.H. Lewis *et al.* (1987). These latter authors give an empirical formula for the probability of complete skin perforation (full-thickness skin laceration) which is said to apply to both primary and secondary fragments (debris).

Experiments were performed using goat skin to simulate human tissue. This approach follows the work of Sperraza and Kokinakis (1968), who found no significant difference between goat and human skin in this respect.

The results were correlated using the logistic equation

$$P(\mathrm{P_{skin}}) = \frac{1}{1 + \exp[-a + bmu^2/A)]} \qquad [17.42.18]$$

where A is the projected area of the fragment (cm^2), m is its mass (g) and u is its velocity (m/s), and a and b are constants.

Values of the constants given for bare skin and for two-layer and six-layer uniforms are:

Target	*Constant*	
	a	b
Bare skin	−28.42	2.94
Two-layer uniform	−49.47	4.62
Six-layer uniform	−50.63	4.51

The corresponding probit equation for bare skin is

$$Y = -20.5 + 1.54 \ln(mu^2/A) \qquad \text{Bare skin} \qquad [17.42.19]$$

where A is the projected area of the fragment (m^2), m is its mass (kg) and u is its velocity (m/s).

Analysis by the authors of the data for skin *in situ* indicated that there is strong evidence to support the adoption of the following thresholds for skin penetration and skin perforation:

$$mu^2/A = 3 \times 10^5 \ \mathrm{J/m^2} \qquad \text{Skin penetration}$$

$$= 3.6 \times 10^5 \mathrm{J/m^2} \qquad \text{Skin perforation}$$

On the basis of these findings a revision was made to the correlation of J.H. Lewis *et al.* (1987). The threshold was taken to be equivalent to a probability of 1%. The probit equation of Lewis *et al.* given in Equation 17.42.19 was revised by adjusting the intercept but retaining the slope. The result for bare skin is

$$Y(\mathrm{P_{skin}}) = -17.0 + 1.54 \ln(mu^2/A) \qquad [17.42.20]$$

The model assumes that on perforation of the skin there is a reduction in the causative factor (mu^2/A) of 360 000 $\mathrm{J/m^2}$, the threshold value for skin perforation. The residual energy is then available for further penetration of the body region in question.

17.42.5 Penetration to vulnerable areas

Head and neck

Information on penetration of the skull by fragments is given in the *Textbook*. A series of 54 shots were made using eight fresh skull caps obtained at autopsy at velocities in the range 280–960 m/s. The data given are for penetration by a 53 mg fragment, and are shown in section A of Table 17.59. It is recommended in the *Textbook* that the crude data for the normal velocity be increased by 10% to allow for experimental error and this adjustment is shown in the second column of the table.

The probit equation obtained from Table 17.59, section A, is

$$Y(\mathrm{P_{skull}}) = -40.5 + 3.03 \ln(mu^2/A) \qquad [17.42.21]$$

Thorax

An essentially similar treatment is available for penetration of the sternum, the information again deriving from the *Textbook*. A series of 56 shots were made using 13 fresh sterna obtained at autopsy at velocities in the range 153–530 m/s. The data given are for penetration by a 53 mg fragment and are shown in section B of Table 17.59. It is recommended in the *Textbook* that the crude data for the normal velocity be increased by 10% to allow for experimental error, and this adjustment is shown in the second column of the table.

The vulnerability of the thorax, given penetration of the skin, is obtained in the model from the vulnerability to perforation of the sternum. A fraction, say two-thirds, of the thorax may be considered to be protected by the sternum or other bones. The remaining one third is treated as unprotected and is lumped with the abdomen. This redistribution is effected by adjusting the values of the MPA A_i used for these two parts of the body.

Then applying to the thorax the probit equation obtained for the sternum from Table 17.59, section B

$$Y(\mathrm{P_{thor}}) = -7.37 + 0.948 \ln(mu^2/A) \qquad [17.42.22]$$

Abdomen

Data given below indicate that 84% of the injuries to the abdomen result in death or serious injury. This value is taken as the probability $P(\mathrm{P_{abd}})$ of penetration to a vulnerable area given perforation of the skin.

Limbs

The vulnerable parts of the limbs are bones and vessels and nerves outside the bone area. The *Textbook* gives the MPA of these vulnerable areas and the probability $P(\mathrm{P_{limb}})$ is then simply the ratio of the vulnerable area of the limb to its total MPA. The data are shown in section C of Table 17.59.

17.42.6 Fatal injury

All parts of body

An approximate estimate of the probability of fatality given fatal or serious injury may be obtained from the data on civilian air raid casualties given in the *Textbook* and shown in section A of Table 17.60. This table gives the overall probability of fatality as 0.26, which may be compared with the value of 0.27 given in the *Textbook* for 'all regions'.

It should be noted that the probability given in this table is the probability of fatality given a hit, not the

Table 17.59 *Penetration of vulnerable areas by fragments*

A Skull[a]

Normal impact velocity (ft/s)	*Adjusted impact velocity,*[b] (ft/s)	*Causative factor* mu^2/A (J/m^2)	*Probability of perforation,* $P(P_{skull})$ (%)
312	343	1.40×10^6	0
408	449	2.40×10^6	12.7
507	558	3.70×10^6	75.2
591	650	5.03×10^6	82.1
769	846	8.52×10^6	100

B Sternum[a]

Normal impact velocity (ft/s)	*Adjusted impact velocity,*[b] (ft/s)	*Causative factor* mu^2/A (J/m^2)	*Probability of perforation,* $P(P_{stern})$ (%)
173	190	0.431×10^6	42.1
220	242	0.697×10^6	77.0
295	325	1.25×10^6	77.0
373	410	2.03×10^6	91.6
519	571	3.88×10^6	100

C Limb

Limb	*Bone* (ft^2)	*MPA Vessels and nerves* (ft^2)	*Vulnerable parts* (ft^2)	*Total* (ft^2)	*Conditional probability of penetration,* $P(P_{vul} \mid P_{skin})$
Upper limb	0.31	0.12	0.43	0.92	0.467
Lower limb	0.55	0.22	0.77	1.65	0.467

[a] Source: *Textbook of Air Armament* (Ministry of Supply, 1952): Table C1. Data for a 3/32 in. sphere, of mass 53 mg.
[b] Adjusted as explained in text.

probability of fatality given penetration to a vulnerable area.

The *Textbook* also gives information on British military casualties in the First World War as given in section B of Table 17.60. These data have been used in relation to fatal injuries of the trunk, as described below.

Head and neck

Further information on fatal injuries arising from penetration of the skull is given by A. Palmer (1962). He gives data on the mass distribution of flak fragments in 30 cases recovered from fatal and non-fatal fracture wounds to the skull. The proportion of the cases which were fatal is 77%. On this basis the probability of fatality given perforation of the skull $P(\mathrm{K} \mid \mathrm{P}_{\mathrm{vul,\,skull}})$ is taken as 0.8.

Thorax and abdomen

For fatal injuries involving the thorax and abdomen use has been made of data given in the *Textbook* on military casualties in the First World War shown in Table 17.60, section B. The effect of an injury to the trunk tends to be serious. From the data in the table the probability $P(\mathrm{K} \mid \mathrm{P}_{\mathrm{vul,\,thor}})$ of fatal injury given penetration to the vulnerable area for the thorax is taken as 0.75 and similarly for the probability $P(\mathrm{K} \mid \mathrm{P}_{\mathrm{vul,\,abd}})$.

Limbs

Palmer also gives information on fatal injuries arising from penetration of vulnerable parts of limbs. He gives data on the mass distribution of flak fragments recovered from fatal and non-fatal extremity fracture wounds. The proportion of the cases which were fatal for the upper limb is 5.9% and for the lower limb 15.4%.

An alternative approach is to utilize the Second World War data given in section C of Table 17.59 and section A of Table 17.60. From these tables it may be inferred that for the upper limb

$$P(\mathrm{K} \mid \mathrm{P}_{\mathrm{vul,\,uplimb}}) = 0.07/0.467$$

$$= 0.15$$

and for the lower limb

$$P(\mathrm{K} \mid \mathrm{P}_{\mathrm{vul,\,lwlimb}}) = 0.14/0.406$$

$$= 0.345$$

Table 17.60 *Fatal injury by a fragment penetrating to a vulnerable area*

A British air raid casualties in the Second World War[a]

Region, i	*Proportion of MPA,* $P(H_i \mid H)$	*Conditional probability of fatal injury* $P(K_i \mid H_i)$
Head and neck	0.12	0.60
Thorax	0.16	0.40
Abdomen	0.11	0.56
Upper limb	0.22	0.07
Lower limb	0.39	0.14

B British military casualties in the First World War[a]

	Proportion of effective wounds in each part of body (%)			*Proportion of fatal or serious injury* (%)	*Conditional probability of fatal injury,* $P(K_i \mid P_{vul,\ i})$
	Dead	*Seriously wounded*	*Slightly wounded*		
Head and neck	25.8	27.8	46.4	53.6	0.481
Thorax	59.6	20.7	19.7	80.3	0.782
Abdomen	61.1	23.1	15.7	84.2	0.726
Upper limb	3.0	36.3	60.7	39.3	0.076
Lower limb	3.9	44.4	51.7	48.3	0.081

[a] Source: *Textbook of Air Armament* (Ministry of Supply, 1952). Section A: Table 3; Section B: Table 2

17.42.7 Effect of advances in medicine

Surveys of battle casualties generally conclude that rapid first aid, medical treatment and modern surgery can greatly reduce mortality from wounds to the extremities, or limbs, although this is of little help in the case of wounds to the head. This is supported by statistics which show US battle deaths from extremity wounds were reduced from about 13% of all deaths in the Second World War to 7.4% in Vietnam.

The probability of fatality given penetration to a vulnerable part of a limb $P(\mathrm{K} \mid \mathrm{Pvul, limb})$ during the Second World War is therefore reduced in the model to half its crude estimated value by taking credit for medical advances.

No other credit for medical advances is taken in the model.

17.42.8 Effect of clothing

Clothing may in principle affect the probability of skin perforation. The work of French and Callender (1962) indicates that although exhibiting a finite threshold velocity for perforation, light clothing is much less resistant than skin. It is assumed in the model that the type of clothing worn by civilians offers very little protection against missiles and hence bare skin criteria are used.

17.42.9 Injury model

The model of injury by fragments may be summarized as follows. The adjusted values of proportion A_i/A of MPA assigned to body region i are:

Body region	A_i/A
Head and neck	0.12
Thorax	0.11
Abdomen	0.16
Upper limb	0.22
Lower limb	0.39
$P(P_{skin})$	Equation 17.42.20 for bare skin

Following skin perforation, X is reduced by $360\,000\,\mathrm{J/m^2}$ to account for the energy expended:

$P(P_{skull})$	Equation 17.42.21
$P(P_{thor})$	Equation 17.42.22
$P(P_{abd})$	$= 0.84$
$P(P_{lwlimb})$	$= 0.467$ from Table 17.59, section C
$P(P_{uplimb})$	$= 0.467$ from Table 17.59, section C
$P(K \mid P_{skull})$	$= 0.8$
$P(K \mid P_{thor})$	$= 0.75$
$P(K \mid P_{abd})$	$= 0.75$
$P(K_{uplimb} \mid P_{vul,\ uplimb})$	$= 0.15$
$P(K_{lwlimb} \mid P_{vul,\ lwlimb})$	$= 0.345$

If allowance is made for medical advances since the Second World War, the last two values become 0.07 and 0.15, respectively.

17.43 Dust Explosions

Another explosion hazard in the process industries is the explosion of flammable dusts. Explosions of dust suspensions have characteristics in common with gas

explosions, but there are also some important differences. Fire and explosions can also occur in dust layers.

Legal requirements for plant handling flammable dusts are given in the Factories Act 1961, Section 31. This section includes the following:

> (1) Where, in connection with any grinding, sieving, or other process giving rise to dust, there may escape dust of such a character and to such an extent as to be liable to explode on ignition, all practicable steps shall be taken to prevent such an explosion by enclosure of the plant used in the process, and by removal or prevention of accumulation of any dust that may escape in spite of the enclosure, and by exclusion or effective enclosure of possible sources of ignition.
>
> (2) Where there is present in any plant used in any such process as aforesaid dust of such a character and to such an extent as to be liable to explode on ignition, then, unless the plant is so constructed as to withstand the pressure likely to be produced by any such explosion, all practicable steps shall be taken to restrict the spread and effects of such an explosion by the provision, in connection with the plant, of chokes, baffles and vents, or other equally effective appliances.

There are other statutory requirements relating to particular flammable dusts.

Accounts of dust explosions are given in *Dust Explosions in Factories* (HSE, 1970 HSW Bklt 22), *Dust Explosions and Fires* (K.N. Palmer, (1973a), *Explosions* (Bartknecht, 1981a), *Dust Explosions* (Cross and Farrer, 1982), *Dust Explosions* (Field, 1982), *Development and Control of Dust Explosions* (Nagy and Verakis, 1983), *Venting Gas and Dust Explosions* (Lunn, 1984b, 1992), *Dust Explosions* (Bartknecht, 1989) *Dust Explosions in the Process Industries* (Eckhoff, 1991) and by Wilkes (1948), Maisey (1965), H.E. Rose (1970, 1975), K.N. Palmer (1971, 1974a–c, 1975a,b, 1975–76, 1977, 1981a, 1982, 1983, 1990), O'Reilly (1972), Schwab (1986) and Lunn (1989a,b, 1990).

Relevant codes are NFPA 68: 1994 *Explosion Venting* and NFPA 69: 1992 *Explosion Prevention Systems*. In addition, there are a number of codes relevant to particular industries which deal with dusts such as NFPA 61 series (foodstuffs), NFPA 654 (chemicals, dyes, pharmaceuticals and plastics), NFPA 655 (sulphur) and NFPA 651 (aluminium and magnesium).

Selected references on dust explosions are given in Table 17.61 and on dust explosibility in Table 17.62.

17.43.1 Industrial dusts

Many industrial materials are at some stage handled as dusts or powders and many final products are in dust/powder form. Some typical industrial dusts/powders are

(1 wood;
(2 coal;
(3 food (e.g. starch, flour, sugar, cocoa, feedstuffs);
(4 chemicals (e.g. drugs, dyestuffs);
(5 plastics (e.g. urea formaldehyde resin, polyethylene, polystyrene);
(6) metals (e.g. aluminium, magnesium).

Some of the operations in which such dusts are produced are considered in Section 17.49.

Table 17.61 *Selected references on dust explosions*

W.M. Jones (1940a,b); Burgoyne (1945); Wilkes (1948); Hartman (1948a, 1950, 1957); Drinker and Hatch (1954); Fishkin and Smith (1964); Schwab and Othmer (1964); Nagy and Surincek (1966 BM RI 6811); Eggleston (1967); Essenhigh (1967); Vegter (1969); HSE (1970 HSW Bklt 22, 1975 SHE 830); H.E. Rose (1970, 1975); FPA (1974 CFSD 6015, 1989 CFSD FS 6021, 6023, 6023, 6024); Kuhnen (1971); Bartknecht (1971, 1972a,b, 1973, 1974a, 1975, 1980, 1981a, 1989); Clague (1972); O'Reilly (1972); Ritter (1972); Hess (1973); Nettleton and Stirling (1973); K.N. Palmer (1973a, 1981a, 1990); FRS (1973 Fire Res. Note 992); Suchan (1973); Anon. (1976 LPB 8, p. 7); Griffith (1978); BRE (1979 TIL 63); Cardillo and Anthony (1979); Deasy (1979); Clavel and Estrabaud (1980); CMI (1980 CMI 790750–1); P.E. Moore (1980); Cross (1981); IBC (1981/13, 1982/23, 1984/49 Pt 2); Jacobsen (1981); Napier (1981); Tait (1981); Cross and Farrer (1982); Field (1982); Moen (1982b); Siwek (1982); Tamanini (1982); Thorne (1982); Wolanski (1982a,b); Zeeuwen (1982, 1988); Nagy and Verakis (1983); Boiko *et al.* (1984); Kauffman *et al.* (1984); Wolanski *et al.* (1984); N. Gibson, Harper and Rogers (1986); Schwab (1986); Cartwright (1987, 1990); NFPA (1989 NFPA 61A, 61B); W.E. Baker, White and Hokanson (1991); Eckhoff (1991, 1993); Godbey (1991); Cashdollar *et al.* (1992); Ural (1992); Anon. (1993 LPB 113, p. 0)

Ignition

Blactin and Robinson (n.d.); Morse (n.d., 1958); Boyle and Llewellyn (1950a,b); Underwriters Laboratories (1953); K.N. Palmer (1957, 1973a, 1976b, 1981b); K.N. Palmer and Tonkin (1957); Chauvin (1973); Eckhoff (1976a,b, 1991); Eckhoff and Enstad (1976); J.F. Hughes and Bright (1979); Anon. (1980 LPB 35, p. 1); Cross (1980); Department of Agriculture (1980); N. Gibson and Rogers (1980); Glor and Boschung (1980); Krishna and Berland (1980); Leuschke (1980, 1981); Dahn (1981); Petino (1981); Cross and Farrer (1982); Zeeuwen (1982); Borisov *et al.* (1984); Hertzberg, Conti and Cashdollar (1985); Pedersen and Eckhoff (1987); Tyler and Henderson (1987); Anon. (1988l); Henderson and Tyler (1988); Bruderer (1989b); FPA (1989 CFSD FS 6023); Schuber (1989); Amyotte, Baxter and Pegg (1990)

Combustion

Cassel, Das Gupta and Guruswamy (1949); Cassel, Liebman and Mock (1957); Essenhigh and Woodhead (1958); Cassel and Liebman (1959); Butlin (1971); Rae (1971); Ishihama and Enomoto (1973, 1975); Eckhoff (1977); Liebman, Conti and Cashdollar (1977); Eckhoff and Mathisen (1978); N. Gibson and Rogers (1980); Kansa and Perlee (1980); Pineau (1982); Tulis and Selman (1982, 1984); Ballal and Lefebvre (1983a,b); Veyssiere (1984); Kauffman *et al.* (1985); Pineau, Chaineaux and Ronchail (1986); Bao-Chun, Fan and Sichel (1988); Proust and Veyssiere (1988); Amyotte and Pegg (1989); D. Bradley, Chen and Swithenbank (1989); Britton and Chippett (1989); Fan and Sichel (1989); Pu, Jarosinksi *et al.* (1989); Pu, Marunkiewicz *et al.* (1989); Aldis and Gidaspow (1990); Zhang and Grönig (1991); Hertzberg *et al.* (1992); Kumar, Bowles and Mintz (1992); Eidelman and Xiaolong Yang (1993); Seung Wook Baek, Kook Young Ahn and Jong Uck Kim (1994)

Particular materials: Underwriters Laboratories (1953); K.N. Palmer (1982); Ogle *et al.* (1988)

Hazardous area classification
Moodie (1971); ICI/RoSPA (1972 IS/91)

Dust fires
K.N. Palmer (1957, 1973a, 1981b, 1983); K.N. Palmer and Tonkin (1957); Verkade and Chiotte (1978a); Leisch, Kauffman and Sichel (1985)

Process plant handling
EEUA (1968 Hndbk 19); R.W. Nelson (1972); K.N. Palmer (1973a, 1975a,b, 1984 LPB 54); Schafer (1973b); Theimer (1973); Pollock (1975); Dressler (1977); Aldis and Lai (1979); J.F. Hughes and Bright (1979); Gillis and Dale (1980); N. Gibson (1981); Hoenig (1981, 1989); Anon. (1988l); Bartknecht (1989); FPA (1989 CFSD FS 6024); Gelfand *et al.* (1989); Siwek (1989b); Eckhoff (1991); Siwek and Cesana (1993); Maddison (1994)
Bags: Bruderer (1993)
Bucket elevators: K.C. Brown (1951); Gillis and Dale (1980); Gillis (1981); Kossebau (1982)
Driers: Reay (1977, 1979 LPB 25); Bartknecht (1981a); Schmalz (1982); Bruderer (1989a); Crowhurst (1989); Abbott (1990)
Dust collectors, filters: K.N. Palmer (1974a); J. Palmer (1980); Bartknecht (1981a); Frank (1981); Reinauer (1981); Cairns (1984); N. Bennett, Cairns and Cooper (1986); van Laar (1993)
Grinding mills: Schmalz (1982)
Silos: Themier (1973); Bartknecht (1981a, 1985); CMI (1982 CMI 813307–1); Eckhoff (1982, 1984, 1991); Eckhoff *et al.* (1982); Radant (1982); Eckhoff *et al.* (1988); Britton and Kirby (1989)
Metal dusts: H. Brown (1941 BM IC 7148)

Explosion prevention and protection
SMRE (Explosion 4); W.M. Jones (1940b); Valentine and Merrill (1942); Burgoyne and Fauls (1963); Burgoyne (1967a); Craven and Foster (1967); K.N. Palmer (1967b, 1973a, 1973 FRS Fire Res. Note 961, 1974a); Coffee (1968); Bartknecht (1971, 1972a,b, 1973, 1974a, 1975, 1977, 1981a,b, 1989); R.W. Nelson (1972); N. Gibson (1973a); Hess (1973); FPA (1974 CFSD FS 6015, 1989 CFSD FS 6022); Cocks (1979); S. Clark (1981); P. Moore (1981); Brennecke (1982); IB (1982/23, 1984/49 Pt 2, 1988/74, 1992/90); Rickenbach (1982); Ritter (1982); Stalder (1982); Wetterich (1982); Wiemann (1982); Ebert (1982/83); Nagy and Verakis (1983); European Information Centre on Explosion Protection (1984); Janssens (1984); Lunn (1984b, 1988a, 1992); Schofield (1984); Butters (1985 LPB 66); BSI (1986); NFPA (1988 NFPA 654, 1992 NFPA 69); Schofield and Abbott (1988); Hoenig (1989); Anon. (1990 LPB 95, p. 7); Amrogowicz and Kordylewski (1991); Amyotte, Mintz and Pegg (1992); Amyottte and Pegg (1992); Ebadat (1993)
VDI 2263: 1990–

Explosion relief
FRS (Fire Res. Note 830, 1973 Fire Res. Note 961); Hartmann (1946); Hartmann and Nagy (1946 BM RI 3924, 1957); Nagy, Zeilinger and Hartmann (1950 BM RI 4636); K.C. Brown (1951); K.C. Brown and Curzon (1962, 1963); K.C. Brown *et al.* (1962); Maisey (1965); Heinrich (1966, 1972, 1974, 1975); K.N. Palmer (1967b, 1971, 1973a, 1974a–c, 1975/76, 1977); Donat (1971a, 1977a); Heinrich and Kowall (1971, 1972); Pineau (1973); Bartknecht (1974a,b, 1977a, 1981a, 1985, 1986, 1989); Pineau, Giltaire and Dangeaux (1974, 1976, 1978); Matsuda and Naito (1975); N. Gibson and Harris (1976); Burgoyne (1977); Hattwig (1977); Nettleton (1977a); Rust (1979); W.E. Baker, Hokanson and Kulesz (1980); M.R. Marshall (1980); BRE (1981 N81/81, N101/81); Eckhoff (1982, 1989, 1990, 1991); Field (1982, 1984); Scholl (1982); Eckhoff and Fuhre (1983); Lunn (1984b, 1989a,b, 1990, 1992); Schofield (1984); IBC (1985/63, 1987/72); Lunn and Cairns (1985); Eckhoff, Fuhre and Pedersen (1986, 1987); Pineau, Chaineaux and Ronchail (1986); Simpson and Woinsky (1986); Eckhoff *et al.* (1988); Lunn, Brookes and Nicol (1988); Lunn, Crowhurst and Hey (1988); Zeeuwen (1988); P. Moore (1990); Siwek (1989a, 1994); M. Epstein *et al.* (1990); Tamanini (1990); Hey (1991); IChemE (1992/33); Siwek, Glor and Torregiani (1992); K. van Wingerden (1993); Scheuermann (1994); NFPA (1994 NFPA 68)
VDI 3673: 1979
Disposal of vented material: K.N. Palmer (1973a); Bartknecht (1981a, 1989)

Explosion suppression
Bartknecht (1971, 1973, 1977b, 1981a,b); Rae and Thompson (1979); P. Moore (1982b, 1984, 1986, 1990); P. Moore and Bartknecht (1986); Senecal (1989a,b); Kordylewski and Amrogowicz (1992)

Hybrid explosions
Cardillo and Anthony (1978); Pellmont (1979, 1982); Kauffman *et al.* (1984); Senecal (1989b); Torrent, Fuchs and Fernandez (1990); Torrent, Fuchs and Borrajo (1991); W.E. Baker, White and Hokanson (1991)

Grain elevators, inc. explosions
Morse (1958); Anon. (1978f); Verkade and Chiotte (1978a,b); Anon. (1979 LPB 27, p. 76); Aldis and Lai (1979); Atallah (1979); Anon. (1980q); Tait, Repucci and Tou (1980); Brasie (1981); Kauffman (1981, 1982, 1986); W.E. Phillips (1981); Winsett (1981); Pedersen and Eckhoff (1987); NFPA (1989 NFPA 61B)

Hazard assessment
Brasie (1981)

Table 17.62 Selected references on dust flammability and explosibility

Wheeler (1935a); Hartmann, Nagy and Brown (1943 BM RI 3722); Hartmann and Nagy (1944 BM RI 3731, RI 3751, 1949, 1957); Underwriters Laboratories (1944); Hartmann and Greenwald (1945); Bowes, Burgoyne and Rasbash (1948); Hartmann (1948a, 1957, 1958); Hartmann, Cooper and Jacobsen (1950 BM RI 4725); Hartman, Nagy and Jacobsen (1951 BM RI 4835); Hartman, Jacobsen and Williams (1954 BM RI 5052); Carpenter (1957); Carpenter and Davies (1958); Dorsett *et al.* (1960 BM RI 5624); Jacobsen *et al.* (1961 BM RI 5753); Nagy and Portman (1961 BM RI 5815); Jacobsen, Nagy and Cooper (1962 BM RI 5971); Maguire, Slack

and Williams (1962); Cassell (1964 BM RI 6651); Jacobsen, Cooper and Nagy (1964 BM RI 6516, 1965 BM RI 6851); W.F. Marshall, Palmer and Seery (1964); Nagy, Cooper and Stupar (1964 BM RI 6561); Nagy, Dorsett and Jacobsen (1964 BM RI 6543); Singer (1964 BM RI 6369); Nagy, Dorsett and Cooper (1965 BM RI 6597); Leuschke (1966); Craven and Foster (1967); W.E. Mason and Wilson (1967); K.N. Palmer (1967a, 1973a,b); Singer, Cook and Grumer (1967 BM RI 6931); Dorsett and Nagy (1968 BM RI 7132); Gillis (1968); HM Factory Inspectorate (1968); Nagy, Cooper and Dorsett (1968 BM RI 7208); Schwab (1968, 1986); Singer, Bruzsak and Grumer (1968 BM RI 7103); Grumer (1971 BM RI 7552); Fris (1972); N. Gibson (1972); Heinrich (1972); Kohlschmidt (1972); Lutolf (1972); Mintschew *et al.* (1972); Novotny, Pantoflicek and Lebr (1972); Raftery (1972, 1975 FRS Fire Res. Tech. Pap. 21); Ishihama and Enomoto (1973); Mitsui and Tanaka (1973); CMI (1975 CMI 72001-12, 1987 CMI 77005-2); Eckhoff (1975, 1976a,b, 1985, 1991); Tonkin (1975 FRS Fire Res. Note 1028); Eckhoff and Enstad (1976); Kelley and Forkner (1976 BM RI 8201); Lovachev (1976, 1978b); Napier (1977b); Burgoyne (1978); Eckhoff and Mathisen (1978); Nettleton (1978a); Hertzberg, Cashdollar and Opferman (1979 BM RI 8360); P.E. Moore (1979a); Scholl *et al.* (1979); Kalkert and Schecker (1980); Nomura and Tanaka (1980); Sinclair and Sweis (1980); Bartknecht (1981a, 1989); Cocks and Meyer (1981); Deguingand and Galant (1981); Hertzberg, Cashdollar and Lazzara (1981); Jacobson (1981); I. Swift (1981, 1982); BRE (1982 CP5/82, 1983 SO 37); Field (1982, 1983, 1985 LPB 66); Hertzberg (1982); Hertzberg *et al.* (1982); Siwek (1982); Zeeuwen (1982, 1988); Felstead, Rogers and Young (1983); Nagy and Verakis (1983); Nomura, Torimoto and Tanaka (1984); Tulis and Selman (1982, 1984); Sweis and Sinclair (1985); Dahn, Ashum and Williams (1986); N. Gibson *et al.* (1986); Sweis (1987); Lunn (1988b); Cashdollar, Hertzberg and Zlochower (1989); M. Ward (1989); Amyotte *et al.* (1991); Continillo *et al.* (1991); Hertzberg, Zlochower and Cashdollar (1991, 1992); Pu *et al.* (1991); Torrent, Fuchs and Borrajo (1991); Cashdollar and Chatrathi (1992); Liu and Katsabanis (1993); Mintz (1993); Zhang and Wall (1993); Cashdollar (1994); Chatrathi (1994); Hensel *et al.* (1994)

Dusts may be formed by condensation from vapours of materials which condense to form solids directly or by mechanical size reduction of solid materials. In the former case the particle size tends to be much smaller.

The terms 'dust' and 'powder' tend to be used interchangeably and have no agreed definition. It is desirable, however, to set some limits to the particle size of materials under consideration. BS 2955: 1958 defines as 'powder' material with a particle diameter of less than 1000 μ (16 BS mesh size) and as 'dust' material with a particle diameter of less than 76 μ (200 BS mesh size). K.N. Palmer (1973a) takes a somewhat wider definition and does not exclude from his treatment information on materials with a particle diameter coarser than 1000 μm.

17.43.2 Dust explosions

The hazard of a dust explosion or fire exists wherever flammable dusts are handled. Generally, a dust explosion occurs only if the dust is dispersed in air, but transition from a fire to an explosion can occur, and vice versa. If a burning dust is disturbed, a dust suspension may be formed and ignited. This initial explosion may generate further dust clouds, which in turn explode. On the other hand, burning particles from an explosion may act as the source of ignition for a fire of other flammable materials.

The explosive effect of a dust explosion is caused by the rapid release of heat and the accompanying rapid pressure rise or expansion of the hot gases.

In dust explosions the combustion process is very rapid. The flame speed is high, comparable with that in gas deflagrations. Maximum explosion pressures are often close to the theoretical values calculated assuming no heat loss during the explosion.

It is uncertain whether detonation can occur in dust explosions in industrial plant. The flame speed in dust explosions is high and in some cases has been reported as approaching that found in detonations. Most of the evidence for detonations in dust suspensions relates to coal mine galleries where the explosion was initiated by a strong ignition source. It is not clear whether detonations can develop from weak ignition sources in industrial plant.

As far as explosion protection is concerned, K.N. Palmer (1973a) states:

> It is general practice in considering protection against dust explosions, in industrial plant, to assume that deflagrations rather than detonations occur. This procedure has proved to be satisfactory in practice, which is fortunate, because deflagrations are simpler to deal with than detonations.

The sequence of events in a serious industrial dust explosion is often as follows. A primary explosion occurs in an item of plant. The explosion protection is not adequate to prevent the flame issuing from the plant, due either to rupture of the plant or to poor explosion venting. The air disturbance disperses the dust in the work room and causes a secondary explosion. The quantity of dust in the secondary explosion often exceeds that in the primary one. Moreover, the building in which the secondary explosion occurs may be weaker than the plant itself. The secondary explosion is thus often more destructive than the primary one.

In some cases the primary explosion also occurs in the open and disturbs dust deposits, and this causes a secondary explosion. In other cases the primary explosion occurs in one unit of the plant and the explosion propagates within the plant to other units.

The possibility of a highly destructive secondary explosion makes dust explosions rather unpredictable.

It is characteristic of plant handling dusts that it is generally very weak relative to the stresses exerted by a dust explosion. Frequently it can withstand pressures of only 7–15 kN/m^2 (1–2 lb$_f$/in.^{2}). This compares with the pressures of up to 1000 kN/m^2 (140 lb$_f$/in.^{2}) which have been reported for dust explosions under the most unfavourable conditions.

Similar considerations apply to buildings containing plants handling dusts. Generally buildings cannot withstand more than about 7 kN/m^2 (1 lb$_f$/in.^{2}) pressure.

Some very destructive dust explosions have occurred in multi-storeyed buildings. The failure of walls on a lower floor has led to collapse of floors and walls on

higher storeys. A particular hazard in multi-storey buildings is vertical bucket elevators handling dust. A bucket elevator may allow an explosion to propagate through many storeys of the building.

The dust explosion problem is aggravated by the increasing size of plants. The damage caused by an explosion in a large volume may be more than prop ortionately greater than that resulting from a small volume explosion, because the larger unit is frequently relatively weaker.

A particular problem arises where it is desired to use plant designed for a low explosibility dust to handle a high explosibility one. In this case it is essential to check very carefully whether the plant is suitable or needs modification.

17.43.3 Dust explosion incidents

Accounts of dust explosion accidents have been given in *Dust Explosions* (D.J. Price and Brown, 1922), in *Report of Important Dust Explosions* (NFPA, 1957/1), in *Dust Explosions in Factories* (HSE, 1970 HSW Blkt 22) and by K.C. Brown and James (1962), Beach (1964), K.N. Palmer (1973a) and Kaufman (1986).

The HSE booklet lists a wide range of industries and operations in which serious dust fires/explosions have occurred. Beach gives a detailed analysis of dust explosions, excluding those in coal mines, in the period 1900–59. He lists 1110 explosions and 648 fatalities.

Some principal dust explosions are given in Table 17.63.

Historically, industries particularly affected by dust explosions have been flour milling, grain storage and coal mining. A classic flour mill explosion was that in a flour mill in Turin in 1785 (Morozzo, 1795). Serious flour mill explosions have occurred in the UK, including one at Bow, London, in 1965 which killed five people.

An explosion in a starch/corn plant at Cedar Rapids, Iowa, in 1919 killed 43 people and one at a similar plant in Peking, Illinois, in 1924 resulted in 42 deaths.

Grain storage facilities are liable to serious dust explosions. In 1977 a series of dust explosions occurred in a set of grain silos at Westwego, near New Orleans, Louisiana, which killed 35 people (Case History A89). This disaster was thus on the same scale as that of Flixborough.

Many severe dust explosions have also occurred in coal mines, but these are not considered here.

Some statistical data on dust explosions are given by Lunn (1992). In the UK in the period 1958–67, there were 247 reported explosions with 9 fatalities and 324 non-fatal injuries, and in the period 1962–79 there were 474 explosions reported with 25 fatalities and 633 non-fatal injuries; 10 of the 25 fatalities in this latter period occurred in two incidents.

Lunn also quotes two other surveys. One is by the HSE covering the periods 1979–84 and 1985–88, and gives breakdowns by type of event, dust involved, equipment involved and ignition source. In the total period 1979–88 there were 36 dust fires with injury, 123 fires with no injury, 41 explosions with injury and 95 explosions with no injury. Principal items of equipment involved were mills, grinders, filters, driers, silos/hoppers and ducts with 51 (17%), 47 (16%), 43 (14%), 19 (6%) and 15 (5%) events, respectively; 95 (31%) events were classified in the category 'other'. The second survey is by the Berufsgenossenschaftliches Institut für Arbeitssicherheit (BIA) and gives breakdowns by plant group, equipment involved and ignition sources.

17.44 Dust Explosibility Characteristics

17.44.1 Dust explosibility parameters

Important explosibility characteristics of dust suspensions are:

(1) explosibility classification;
(2) minimum explosive concentration;
(3) minimum ignition temperature;
(4) minimum ignition energy;

Table 17.63 *Some dust explosion incidents*

Date	*Location*	*Material*	*Plant/building*	*Deaths/injuries*
1911	Glasgow, UK			5d, 8i
	Liverpool, UK			37d, 100i
	Manchester, UK			3d, 5i
1913	Manchester, UK			3d, 5i
1919	Cedar Rapids, IA	Corn starch	Starch plant	43d
1924	Peking, IL	Corn starch	Starch plant	42d
1930	Liverpool, UK			11d, 32i
1941	Liverpool, UK			6d, 40i
1944	Kansas City, KS	Grain dust	Corn mill	4d, 20i
1955	Waynesboro, GA	Grain dust	Feed plant	3d, 13i
1962	St Louis, MO	Grain dust	Feed plant	2d, 34i
1964	Paisley, UK			5d, 2i
1965	Bow, London, UK	Flour	Flour mill	5d
1970	Kiel, FRG	Grain dust	Grain silo	6d, 18i
1977	Galveston, TX	Grain dust	Grain silo	15d
1977	Westwego, LA	Grain dust	Grain silo	36d, 10i
1979	Hamburg, FRG	Grain dust	Grain silo	2i
1979	Lerida, Spain	Grain dust	Grain silo	7d
1980	Naples, Italy	Grain dust	Grain silo	8i

(5) maximum permissible oxygen concentration to prevent ignition;
(6) mxplosion pressure characteristics –
  (a) maximum explosion pressure,
  (b) maximum rate of pressure rise,
  (c) average rate of pressure rise.

An account is given first of the factors which influence dust explosibility, then of the tests used to determine the explosibility parameters and then of the explosibility parameters themselves.

17.44.2 Factors influencing dust explosibility

The explosibility of dust suspensions in air is characterized by parameters similar to those which define the flammability of gas–air mixtures as described in Chapter 16, but there are some significant differences.

An account is given here of some of the factors which influence the explosibility of the dust itself. Other factors which influence the development of an explosion in a vessel are considered below.

The explosibility of a dust may be regarded as increasing as the minimum explosible concentration, the minimum ignition temperature and the minimum ignition energy decrease and the burning velocity and maximum rate of pressure rise increase.

The characterization of particles is a complex matter, but in general characteristics which affect the behaviour of particles include those of the individual particle itself such as particle composition, density, size, shape, surface properties and moisture content and those of the bulk powder such as bulk density and flow properties.

Some factors which influence dust explosibility are:

(1) chemical composition;
(2) particle size;
(3) moisture content;
(4) oxygen concentration;
(5) inert gas;
(6) admixed inert dust concentration.

Nagy and Verakis (1983) give a large number of plots showing the effect of these factors on the dust explosibility parameters, mainly for particular dusts.

There are certain chemical groups such as COOH, OH, NH_2, NO_2, C≡N, C═N and N═N which tend to be associated with higher dust explosibility and certain others such as Cl, Br and F with lower explosibility.

Dusts of pure metals generally react with air to form metallic oxides. In this case the explosive increase pressure is due to expansion of the nitrogen of the air caused by the heat release. In some cases metals actually react violently with the nitrogen itself to form a metallic nitride.

Volatile matter in the dust tends to enhance the explosibility, although there is generally little increase for volatile contents below 10%. Coal dust in particular can contain a high proportion of volatile matter.

Interestingly, according to Nagy and Verakis, pure carbon dust does not explode. They speculate that the reaction rate of pure carbon with oxygen is too low. But carbon dust containing 8% volatile matter is explosive.

If the dust contains inert material this reduces its explosibility. Some polymeric materials contain inert fillers.

Dust explosibility is strongly affected by particle size. Particle size is usually defined in terms of an equivalent particle diameter. Generally, a dust with a particle diameter greater than 500 μm is unlikely to be responsible for initiation of an explosion, though it may undergo combustion in one already occurring. At the other end of the range, reduction in particle size below about 50–74 μm does not normally result in any significant increase in explosibility. The particle diameter of dusts used in dust explosibility testing normally does not exceed 75 μm.

A dust usually contains a range of particle sizes. A relatively small proportion of fine particles enhances the explosibility of a dust. Moreover, it should be borne in mind that attrition caused by handling the dust tends to generate fine particles.

Figure 17.112 illustrates the effect of particle size on some of the more important dust explosibility parameters. It should be noted that the results are for atomized aluminium, which is a rather extreme case, but nevertheless they illustrate general trends.

Moisture content has a strong effect on dust explosibility, although the effect is generally weak for moisture contents below 10%. At the other end of the range, dust with a moisture content greater than 30% is unlikely to be responsible for initiation of an explosion.

The oxygen concentration in the surrounding atmosphere has a strong effect on dust explosibility, which increases as the oxygen concentration increases. Conversely, the explosibility decreases as the oxygen concentration decreases and the inerts concentration increases.

Dust explosibility is affected by the concentration of any admixed inert dust, although the effect is generally weak for inert dust concentrations below 10–20%.

17.44.3 Dust explosibility tests

The tests which are carried out on dust explosibility vary between countries and a large variety of tests are in use. It is convenient to start with those developed at the Bureau of Mines in the USA, since these have also been widely used in other countries also, including the UK.

Accounts of the various tests in the Bureau of Mines (BM) scheme have been given in a series of reports, in particular that by Dorsett *et al.* (1960 BM RI 5624). A summary has been given by Nagy and Verakis. Some of the apparatus used in these tests is illustrated in Figure 17.113.

Dust explosibility is determined in the Hartmann vertical tube apparatus, shown in Figure 17.113(a). The Hartmann apparatus is a vertical tube of volume 1.2 litre. The dust is dispersed by an air blast. The ignition source is a hot wire or spark igniter. Any propagation of flame is observed. If flame propagation occurs, the dust is explosible.

Two other types of apparatus which are also used to determine whether a dust is explosible are the horizontal tube apparatus and the inflammator apparatus, shown in Figure 17.113(b) and (c), respectively. In the horizontal tube apparatus, the dust is dispersed by an air blast. The ignition source is a hot coil. Any propagation of flame is observed. In the inflammator apparatus, the dust suspension is injected into the apparatus against a deflector plate and falls onto the ignition source. This is a hot wire or spark igniter. Any propagation of flame is observed.

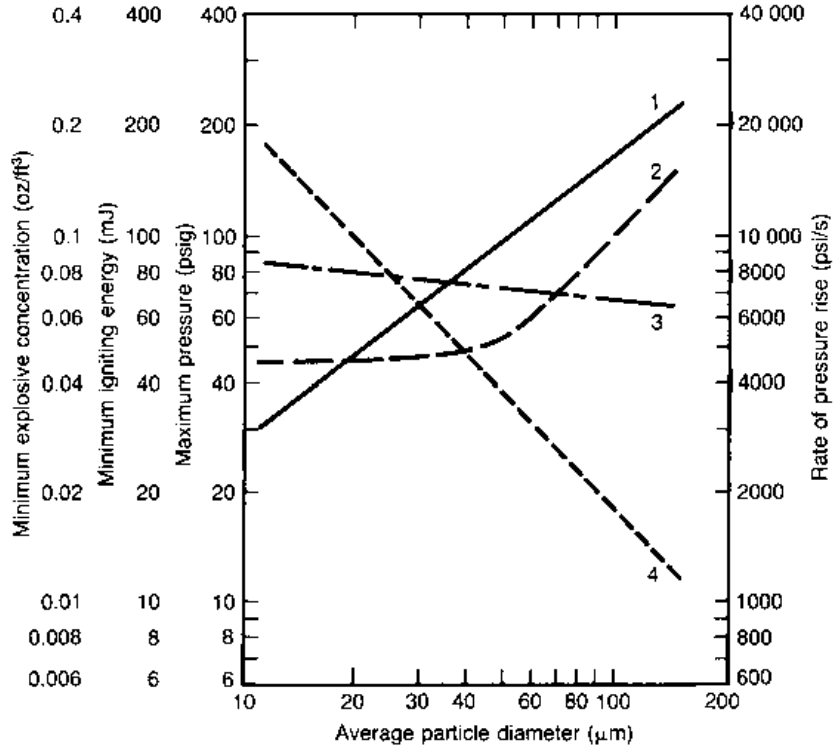


Figure 17.112 *Dust explosibility characteristics: effect of particle size on some principal parameters for atomized aluminium (Nagy and Verakis, 1983). 1, minimum ignition energy; 2, minimum explosive concentration; 3, maximum explosion pressure; 4, maximum rate of pressure rise*

The apparatus is useful for dusts which are not readily dispersed.

The minimum ignition temperature for explosion of a dust suspension is measured in the Godbert–Greenwald furnace, shown in Figure 17.113(d). A dust suspension is injected into a vertical tube held in a constant temperature furnace and the appearance of flame at the open bottom mouth of the furnace is observed.

A separate determination is made of the minimum ignition temperature of a dust layer, which in general differs from that of the dust in suspension. Again the Godbert–Greenwald furnace is used, but in this case the dust is held in a wire mesh basket 1 in. in diameter and $\frac{1}{2}$ in. deep. Another method which is also used is ignition of the layer on a hot plate.

The minimum ignition energy for explosion of a dust suspension is measured in the Hartmann vertical tube apparatus. The dust is dispersed by an air blast. The ignition source is a capacitor discharge spark igniter. Any propagation of flame is observed.

The maximum oxygen concentration to prevent ignition is measured in the open Hartmann vertical tube using spark ignition and in the Godbert–Greenwald furnace.

The pressure–time profile is measured in a closed Hartmann vertical tube apparatus, or Hartmann bomb. The explosion pressure characteristics are obtained from this.

The Hartmann test for the pressure–time profile is the subject of ASTM E789–81 1981 *Test for Pressure and Rate of Pressure Rise for Dust Explosions in a Closed Vessel (Hartmann test)*.

In the UK dust explosibility testing is done at the Fire Research Station (FRS), Borehamwood, and the test scheme covers the explosibility characteristics listed above. These tests have been described by K.N. Palmer (1973a), Raftery (1975 FRS Fire Res. Tech. Pap. 21) and Field (1982).

Dust explosibility classification is performed using the vertical tube, the horizontal tube and the inflammator apparatus. The dust is classed as explosible if a positive result is obtained in any one of the three types of test. The minimum explosive concentration is measured in the vertical tube apparatus, the minimum ignition temperature in a modified form of the Godbert–Greenwald furnace and the minimum ignition energy in a modified form of the vertical tube apparatus.

The maximum oxygen concentration to prevent ignition used to be measured in the Godbert–Greenwald furnace but is now measured in the vertical tube apparatus at ambient temperature. The dust is dispersed by a blast of the reduced oxygen mixture. The ignition source is a hot coil or spark igniter. Any propagation of flame is observed.

The explosion pressure parameters are obtained by measuring the pressure–time profile in a stronger form

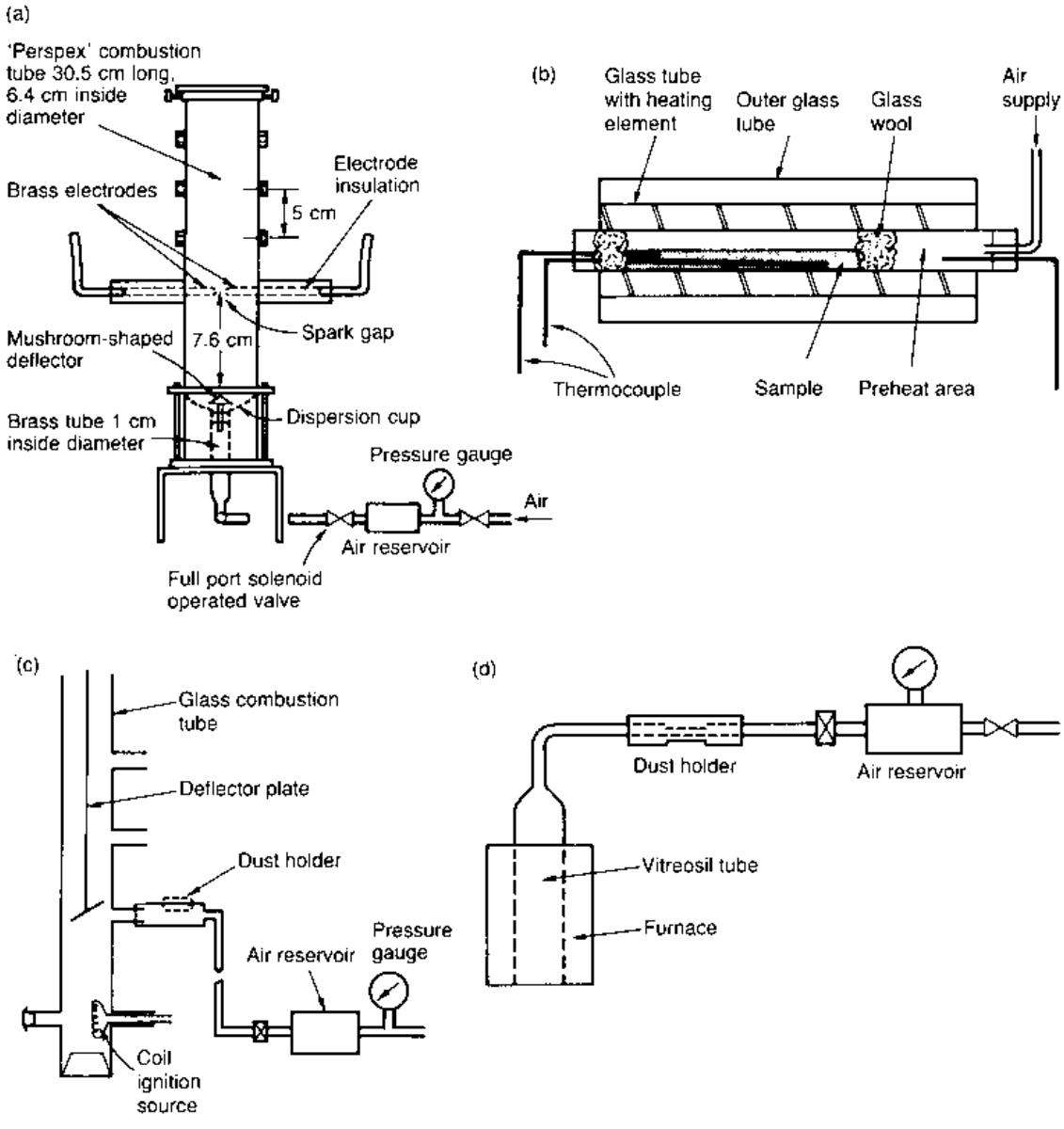


Figure 17.113 *Dust explosibility characteristics – Bureau of Mines test apparatus (Cross and Farrer, 1982): (a) Hartmann vertical tube apparatus; (b) horizontal tube apparatus; (c) inflammator apparatus; (d) Godbert–Greenwald furnace (Courtesy of Plenum Publishing Corporation)*

of the vertical tube apparatus. A typical pressure–time curve, given by K.N. Palmer (1973a), is shown in Figure 17.114. The pressure p_1 is caused by the entry of dispersing air into the vessel. The maximum explosion pressure p_{max} is normally calculated as

$$p_{max} = p_2 - p_1 \qquad [17.44.1]$$

An alternative definition is

$$p_{max} = \frac{p_o}{p_1 + p_o}(p_2 - p_1) \qquad [17.44.2]$$

where p_{max} is the maximum explosion pressure, p_o is atmospheric pressure, p_1 is the small initial pressure rise, and p_2 is the pressure defined in Figure 17.114.

Since p_1 is usually about 40 kPa, the values of p_{max} calculated from Equation 17.44.2 differ by about 40% from those calculated from Equation 17.44.1. In using values of maximum explosion pressure given in the literature, care should be taken to check the definition used.

The maximum rate of pressure rise $(dP/dt)_{max}$ is determined from the maximum slope of the pressure rise

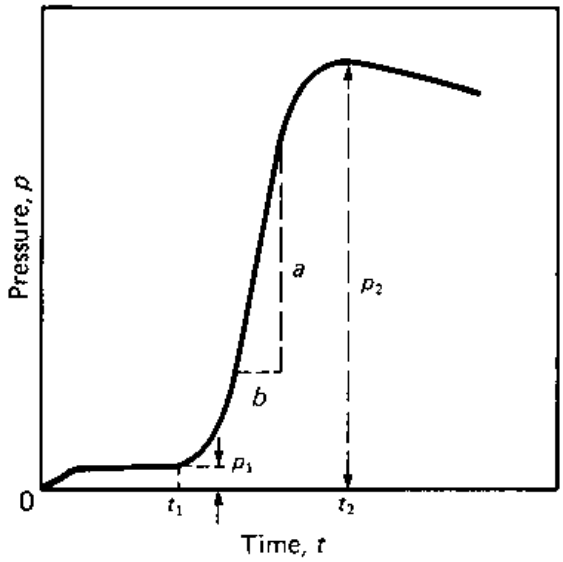


Figure 17.114 *Dust explosibility characteristics: explosion pressure curve in a vertical tube apparatus (K.N. Palmer, 1973a) (Reproduced with permission from* Dust Explosions and Fires *by K.N. Palmer, 1973, Chapman and Hall)*

curve a/b and the average rate of pressure rise $(dP/dt)_{av}$ is calculated as $(p_2 - p_1)/(t_2 - t_1)$.

Another important dust explosibility test scheme is that developed in Switzerland by Bartknecht. Accounts are given by Bartknecht (1981a) and Field (1982). Various workers have shown that the Hartmann vertical tube test involves wall effects and gives less than ideal dust dispersion. In this scheme, therefore, basic test for dust explosibility is performed in a 20 litre spherical vessel, shown in Figure 17.115. This test is an alternative to the Hartmann vertical tube test in the BM scheme.

In the 20 litre sphere test the dust is injected into the sphere from a separate container. The ignition source is located in the centre of the sphere and is usually a chemical igniter with an ignition energy of 10 kJ. A standard time delay is used between injection and ignition.

The 20 litre sphere test is used, like the Hartmann vertical tube, for both qualitative and quantitative determinations. It is used both to determine whether a dust is explosible and to measure the maximum explosion pressure and the maximum rate of pressure rise.

Use is also made of a $1\,m^3$ sphere as an alternative to the 20 litre sphere.

The general approach taken in this scheme is to use these spheres to determine also the other explosibility characteristics. Thus the spheres are used to determine the minimum explosible concentration and the minimum ignition energy.

The analysis of the results is similar to that used for gas explosions. The cube root law is written in the form

$$\left(\frac{dP}{dt}\right)_{max} V^{\frac{1}{3}} = K_{st} \qquad [17.44.3]$$

where K_{st} is the dust explosibility constant (or K_{st} value), P is the absolute pressure, t is time and V is the volume of the vessel. The K_{st} value is the basis of the dust explosibility classification and is a measure of the maximum rate of pressure rise. It corresponds to the K_G value for gases.

Another dust explosibility test scheme is that developed by Eckhoff at the Christian Michelsen Institute (CMI) in Norway. An account is given by Field (1982). Eckhoff has shown that the minimum ignition energy obtained in a test apparatus depends critically on the ignition source used. He has developed for this test an ignition source with a long duration spark which is a particularly efficient igniter for dusts.

Dust explosibility testing in Germany is performed by the Bundesanstalt für Materialprüfing (BAM). Accounts of the test scheme have been given by Leuschke (1966) and Field (1982). For dust explosibility use has been made of the vertical tube and inflammator types of apparatus, but increasing use is made of the 20 litre and $1\,m^3$ spheres. Other parameters such as minimum explosive concentration and minimum ignition energy are determined in relatively large ($\sim 1\,m^3$) vessels.

Turning to the background to, and interpretation of, these various tests, the two main apparatus for dust explosibility testing are the Hartmann vertical tube and the 20 litre sphere. The Hartmann tube is liable not to give uniform conditions for dust dispersion and turbulence. Further, it is subject to wall effects. After initial spherical expansion the flame travels as two fronts up and down the tube. These conditions give a lower rate of combustion and of pressure rise. Consequently the strength of the pressure rise in the Hartmann bomb is less than that in the 20 litre sphere.

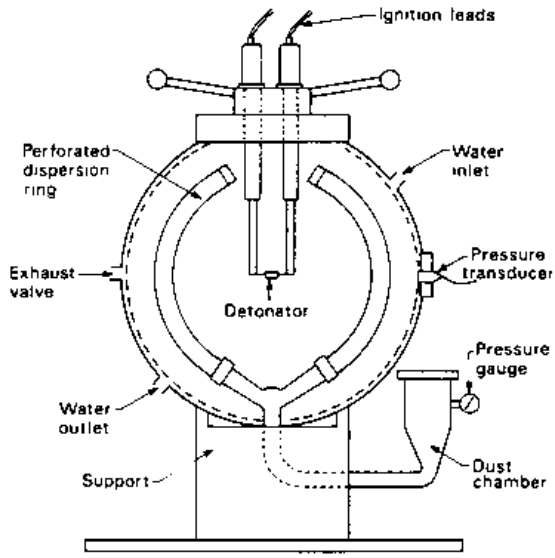


Figure 17.115 *Dust explosibility characteristics: 20 litre sphere test apparatus (Field, 1982; reproduced by permission of Elsevier Science Publishers)*

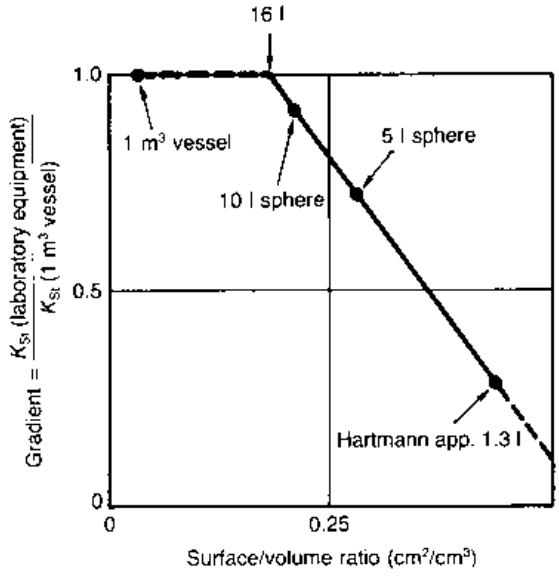


Figure 17.116 *Dust explosibility characteristics: effect of test vessel size on K_{st} value (Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

These problems are largely overcome by the use of a sufficiently large spherical test vessel. The two principal vessels adopted are 20 litre and 1 m^3 spheres. It has been shown that the former is close to the critical size below which effects of vessel size occur and above which they do not. This is illustrated in Figure 17.116.

A large amount of the earlier work on dust explosibility was done at the Bureau of Mines using the Hartmann apparatus. Much recent work has been done using the 20 litre vessel. Moreover, methods have been developed for dust explosion venting which depend on experimental data for one or other apparatus. It is therefore of some interest to be able to relate the results obtained in one apparatus to those obtained in the other. Unfortunately, the results often do not agree and may even give different rankings.

The problem of relating results for the two methods has been examined by Field and Abrahamsen (1981 BRE N81/81). They conclude that there is no simple relation, although Field (1982) does quote the table given in NFPA 68: 1978 relating the dust class to the maximum rate of pressure rise in the Hartmann apparatus; this relation is given below.

The furnace apparatus for the determination of the minimum ignition temperature gives a relatively short residence time. Cross and Farrer comment that a lower minimum ignition temperature may be possible if the dust suspension is held at an elevated temperature for a prolonged period.

With regard to the minimum ignition energy, it has gradually become clear that the Hartmann vertical tube has a number of deficiencies. The test appears to overestimate the minimum ignition energy by a factor of between 2 and 5, and is therefore not conservative.

The ignition source in the Hartmann vertical tube test is a capacitive spark igniter. This has two disadvantages. One is that the spark energy tends to be less than the theoretical energy ($\frac{1}{2}CV^2$) due mainly to loss in the transformer. The other is that it is not possible to control the duration of the spark, which is a significant variable.

An alternative igniter is the direct capacitive spark, which uses a circuit without a transformer, and the inductive spark, developed by Eckhoff. Both these igniters give much lower values of the minimum ignition energy than the Hartmann apparatus. Thus the Hartmann apparatus, the direct capacitance and Eckhoff igniters give for the value of the minimum ignition energy of wheat dust 40, 25 and 7 mJ and for that of fine aluminium powder 1–15, 7.5 and 1 mJ, respectively.

All early data on minimum ignition energy are likely to have been determined using the Hartmann vertical tube test.

The maximum oxygen concentration to prevent ignition was originally measured, as stated above, using the furnace test, but since the operating temperature of the furnace is high and since this concentration is a function of temperature, the values obtained were excessively low. In the UK the measurement is now made using the vertical tube apparatus at ambient temperature. Typical values of the maximum oxygen concentration obtained using the furnace test are 4–7% compared with 10–15% using the vertical tube test.

17.44.4 Dust explosibility classification

In the UK the dust explosibility classification used over a number of years is:

Group A Dusts which ignited and propagated flame in the test apparatus
Group B Dusts which did not propagate flame in the test apparatus

Tests are made using all three types of apparatus described, and the dust is classified as group A if flame propagation occurs in any one apparatus.

Group A dusts should be regarded as capable of causing a dust explosion. Group B dusts are non-explosible, but can burn.

The classification into Groups A and B applies only to dust dispersions at near atmospheric temperature. At higher temperatures some dusts in Group B may be capable of causing a dust explosion.

This classification system replaced an earlier scheme in which dusts were classified as Class I, II or III. Broadly, class I corresponds to Group A and Classes II and III to Group B.

In the USA the NFPA classification of hazardous materials is class I for gases and vapours and Class II or dusts. The latter are subdivided into E, metal dusts, F, carbonaceous dusts, and G, flour dusts.

The Bureau of Mines has developed an index of explosibility which ranks dusts relative to Pittsburgh coal. The index of explosibility IE is the product of the explosion severity ES and the ignition sensitivity IS

$$IE = IS \times ES \qquad [17.44.4]$$

with

$$IS = \frac{(MIT \times MIE \times MEC)_{Pc}}{(MIT \times MIE \times MEC)_{sample}} \quad [17.44.5]$$

$$ES = \frac{(MEP \times MRPR)_{Pc}}{(MEP \times MRPR)_{sample}} \quad [17.44.6]$$

where MEC is the minimum explosive concentration, MEP is the maximum explosion pressure, MIE is the minimum ignition energy, MIT is the minimum ignition temperature and MRPR is the maximum rate of pressure rise, and the subscripts Pc and sample denote Pittsburgh coal and sample.

The index of explosibility is a relative one, and is to this extent less dependent on the apparatus used, but its determination requires the conduct of the full range of tests.

The K_{st} method has already been described. The actual K_{st} classification, its relationship to Hartmann bomb data and to some typical industrial dusts are given in Table 17.64.

17.44.5 Minimum explosive concentration

A dust suspension in air is usually explosible only within certain concentration limits. The upper concentration limit, however, is ill-defined. The lower limit is known as the minimum explosive concentration or the lower explosive limit (LEL), the two terms being interchangeable, and the upper as the upper explosive limit (UEL).

It is found empirically that for a large number of dusts the lower explosive limit lies in the range 20–60 g/m^3 and the upper explosive limit in the range 2–6 kg/m^3.

Some progress has been made in the theoretical estimation of the explosive limits for dusts.

The minimum explosive concentration decreases as the particle size decreases and the volatile matter content and oxygen concentration increase and increases as the moisture content and concentration of admixed inert dust increase.

Dust suspensions in industrial plant are often above the upper limit, but it is not generally practical to use this as a design parameter. For design it is the minimum explosible concentration which is of prime interest.

17.44.6 Minimum ignition temperature

The minimum ignition temperature decreases as the particle size decreases and the volatile matter content and oxygen concentration increase and increases as the moisture content and concentration of admixed inert dust increase.

17.44.7 Minimum ignition energy

The minimum ignition energy decreases as the particle size decreases and the volatile matter content and oxygen concentration increase and increases as the moisture content and concentration of admixed inert dust increase.

17.44.8 Maximum permissible oxygen concentration

There appears to be relatively little data on the variation of the maximum oxygen concentration to prevent ignition with the various influencing factors. As already described, the maximum oxygen concentration decreases as temperature increases.

Table 17.64 *Dust explosibility characteristics: the K_{st} classification*

A Dust explosion classes

Dust explosion class	K_{st}[a] (bar m/s)	*Explosion features*
St 0	0	No explosion
St 1	>0–200	Weak
St 2	201–300	Strong
St 3	>300	Very strong

B Relation of K_{st} and Hartman bomb data[b]

K_{st}[a] (bar m/s)	*Hartman bomb,* $(dP/dt)_{max}$ (psi/s)
≤200	≤7300
201–300	7300–22 000
>300	>22 000

C Typical dusts[c]

Dust explosion class	*Typical dust*
St 0	Non-explosive dust
St 1	Grain dust
St 2	Organic pigment
St 3	Fine metal dust

[a] These figures are for a strong ignition source (10 000 J). For a weak ignition source (10 J) the corresponding figures are given by NFPA 68: 1978 as: 0, >0–100, 101–200 and >200.
[b] NFPA 68: 1978.

17.44.9 Maximum explosion pressure

The maximum explosion pressure increases as the particle size decreases, but the effect is relatively weak. There does not appear to be much data on the effect of the other influencing factors.

17.44.10 Maximum rate of pressure rise

The maximum rate of pressure rise increases as the particle size decreases and the volatile matter content and oxygen concentration increase and decreases as the moisture content and concentration of admixed inert dust increase.

An investigation of the relationship between the initial and maximum rate of pressure rise in dust explosibility testing using a 1 m^3 vessel has been described by Chathrathi (1994). No such relationship was found.

17.44.11 Burning velocity

Another parameter of interest in relation to dust explosions is the burning velocity. Knowledge of this parameter would allow the use of the large number of methods and models developed for gas explosions and gas explosion venting. The burning velocity is not the subject of standard tests, but some work has been done to estimate burning velocities of dusts.

Table 17.65 *Dust explosibility characteristics: relation between maximum rate of pressure rise in Hartmann bomb and burning velocity (after Burgoyne, 1978) (Courtesy of the Society of Chemical Industry)*

Gas	*Maximum rate of pressure rise* (bar/s)	*Maximum burning velocity* (m/s)
Methane	181	0.37
Propane	248	0.46
Ethylene	536	0.70
Hydrogen	1276	3.35

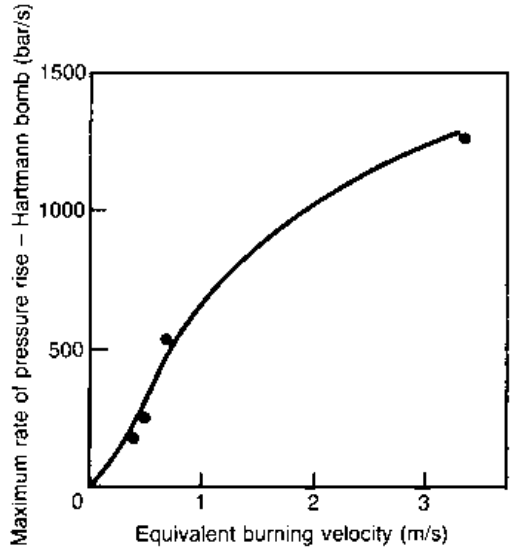


Figure 17.117 *Dust explosibility characteristics: relationship between maximum rate of pressure rise in the Hartmann bomb and burning velocity (Field, 1982; reproduced by permission of Elsevier Science Publishers)*

Maisey (1965) has used an 'equivalent burning velocity' for dust mixtures. His basic approach is to compare the maximum rate of pressure rise for dust mixtures with that obtained for gases with known burning velocity and thus to calibrate the dusts.

Burgoyne (1967a, 1978) has tabulated for gases maximum rates of pressure rise determined in the Hartmann bomb and burning velocities for gases. His data are shown in Table 17.65. These data have then been used by Field (1982) to give the relation between maximum rate of pressure rise in the Hartmann bomb and burning velocity shown in Figure 17.117.

Nagy and Verakis (1983) have given values of the burning velocity of dust mixtures obtained by applying Equation 17.7.77, which gives a relation between the rate of pressure rise and the burning velocity, to the experimental data on the rate of pressure rise of such mixtures determined in work at the Bureau of Mines.

17.44.12 Minimum ignition temperature of dust layer

The minimum ignition temperature of a dust layer is a function both of the dust and of the thickness of the layer, the ignition temperature decreasing as the thickness of the layer increases.

The two methods of measurement, by furnace and by hot plate, give results which differ by up to about 30°C.

The layer ignition temperature decreases as the particle size decreases and the volatile matter content and oxygen concentration increase.

In Germany, use is made of a maximum permissible surface temperature (MPST) for equipment on which dust may settle. An account of work related to this is given by Hensel *et al.* (1994). The MPST is established by determining the glow temperature of the dust and substracting a safety margin, set at 75°C. The glow temperature is the temperature at which a 5 mm dust layer is ignited in a hot plate test. As indicated, a dust layer thicker than 5 mm may give a lower glow temperature. The authors describe work on models based on constant surface temperature and the alternative of constant surface heat flux, utilizing thermal explosion theory.

17.44.13 Hybrid dust–gas mixtures

If flammable gas is present in addition to the dust, the explosibility of the dust is enhanced. Increase in the concentration of flammable gas results in decrease in the minimum explosive concentration, minimum ignition temperature, minimum ignition energy and the increase in maximum rate of pressure rise.

The presence of flammable gas can therefore render explosive a dust–gas mixture at a dust concentration which is below the normal lower explosive limit for the dust and at a gas concentration below the normal lower explosive limit for the gas. Another important effect is to make explosive a dust with a particle size large enough to keep it normally non-explosive.

For such hybrid dust–gas mixtures Cardillo and Anthony (1978) have applied Le Chatelier's equation in the form

$$\frac{c_d}{l_d} + \frac{c_g}{l_g} = 1 \qquad [17.44.7]$$

where c is the concentration (g/m^3) and l is the lower explosive limit (g/m^3) and subscripts d and g denote dust and gas, respectively. They modify this relation empirically to give

$$\frac{c_d}{l_d} + \frac{c_g}{l_g} = 0.8 \qquad [17.44.8]$$

An alternative relation has been given by Pellmont (1979) as follows:

$$l_{dh} = l_d\left(\frac{c_g}{l_g} - 1\right)^2 \qquad [17.44.9]$$

where l_{dh} is the lower explosive limit of the dust given the presence of flammable gas.

Where the hybrid mixture arises due to contamination of a dust by solvent, it is convenient to be able to express Equation 17.44.8 in terms of the mass of solvent contaminated dust and of the mass fraction of solvent in

Table 17.66 *Some explosibility properties of selected dusts (K.N. Palmer, 1973a) (Data in this table from Dust Explosions and Fires, by K.N. Palmer are reproduced with permission of the author and of the publishers, Chapman & Hall)*[a]

Dust	*Minimum explosible concentration* (g/l)	*Minimum ignition temperature*		*Minimum ignition energy* (mJ)	*Maximum permissible oxygen concentration to prevent ignition* (% v/v)	*Maximum explosion pressure* ($lb_f/in.^2$)	*Maximum rate of pressure rise* ($lb_f/in.^2\,s$)	*Average rate of pressure rise* ($lb_f/in.^2\,s$)
		Cloud (°C)	*Layer* (°C)					
Aluminium, atomized	0.045	650	760	50	–	84	>20 000	3 500
Carbon, activated	0.100	660	270	–	–	92	1 700	–
Cellulose acetate	0.035	340	–	20	5	114	6 500	2 800
Coal, 37% volatile	0.055	610	170	60	–	90	2 300	–
Magnesium	0.030	560	430	40	–	116	15 000	–
Nylon	0.030	500	430	20	6	95	4 000	–
Phthalic anhydride	0.015	605	Melts	15	11	72	4 200	1 300
Polyethylene	0.020	390	–	10	–	80	7 500	–
Polystyrene	0.020	500	500	15	–	100	7 000	2 400
Sawdust	–	430	–	–	–	97	2 000	–
Sugar	0.045	370	400	30	–	109	5 000	1 600
Sulphur	0.035	190	220	15	–	78	4 700	1 700
Trinitrotoluene	0.070	–	–	75	–	63	2 100	–
Urea formaldehyde resin	0.020	430	–	34	–	110	1 600	–
Wheat flour	0.050	380	360	50	–	109	3 700	–
Wood flour	0.050	430	–	20	7	94	8 500	–

Sources: All properties except average rate of pressure rise: K.N. Palmer (1973a). Average rate of pressure rise: HSE (1970 Bklt 22).

[a] See text for discussion of higher values of parameters such as maximum explosion pressure and maximum rate of pressure rise obtained in modern test apparatus.

that dust. Thus, following Field (1982), Equation 17.44.8 can be rearranged to yield

$$m_{sd} = \frac{0.8 l_d}{1 + \phi_s[(l_d/l_g) - 1]} \quad [17.44.10]$$

where m_{sd} is the mass concentration of solvent contaminated dust (g/m^3) and ϕ_s is the mass fraction of solvent in that dust.

As already mentioned, the presence of flammable gas also affects the other explosibility characteristics. In particular, it affects the maximum rate of pressure rise and hence the K_{st} value. Bartknecht gives data showing the effect of different concentrations of methane and propane on the dust explosion class of polyvinyl chloride dust. Dust of class St 0 changes to classes St 1, 1/2, 2 and 3 at methane concentrations of 1, 3, 5 and 7%, respectively, and to classes 1, 2/3 and 3 at propane concentrations of 0.9, 2.7 and 4.5%, respectively.

For hybrid mixtures the minimum ignition energy is also lower than that of the dust alone.

17.44.14 Dust explosibility data

There are available a number of compilations of dust explosibility data. Most of these data derive either from the work of the Bureau of Mines (BM) or from that of Donat and Bartknecht.

The explosibility classification of a number of dusts is given in SHW 830 *Dust Explosions in Factories. Classification List of Dusts that have been Tested in the form of a Dust Cloud* by HM Factory Inspectorate (1968).

Compilations of data have been given by Maisey (1965), K.N. Palmer (1973a), Cross and Farrer (1982), Field (1982) and Nagy and Verakis (1983). Field gives two tables, one for data obtained in tests in small scale apparatus and one for data from large apparatus.

Some explosibility properties of selected dusts in air are given in Table 17.66.

The more modern apparatus such as the 20 l vessel tends to yield much high values for the maximum explosion pressure and the maximum rate of pressure rise. A comparison of values is given by Nagy and Verakis (1983).

An account of current results from dust explosibility testing at the BM, using the 20 l vessel and covering a wide and representative range of dusts, has been given by Cashdollar (1994).

17.44.15 Variability of dust explosibility data

Like the data on flammability characteristics, data on dust explosibility exhibit considerable variability. Nagy and Verakis (1983) begin their account with a table of data to emphasize the point. Another set of data illustrating the data variability are those given by Cross and Farrer (1982) on polyethylene.

It may be expected that the considerable progress made in dust explosibility testing has reduced this variability, but it should always be borne in mind, particularly in assessing data for early work.

17.45 Dust Ignition Sources

An account of ignition sources was given in Chapter 16 with particular reference to ignition of gases. The ignition sources for dusts are broadly similar, although there are certain points specific to dusts and dust-handling plant. The account given here is therefore relatively brief.

Discussions of ignition for dusts are given by K.N. Palmer (1973a), Field (1982), Cross and Farrer (1982) and Eckhoff (1991).

Some principal ignition sources for dusts include:

(1) flames and direct heat;
(2) hot work;
(3) incandescent material;
(4) hot surfaces;
(5) electrostatic sparks;
(6) electrical sparks;
(7) friction sparks;
(8) impact sparks;
(9) self-heating;
(10) static electricity;
(11) lightning.

As with gases, it is not easy to compare ignition effects. Different ignition sources are naturally characterized by different quantities such as temperature, energy and power, as reflected in the laboratory tests performed, so that comparison of different ignition sources is difficult. However, in general terms, dusts can be ignited by low energy as well as high energy ignition sources.

Ignition sources which can occur inside the plant are of particular importance. They include incandescent material, hot surfaces, sparks, self-heating and static electricity.

Some account of the control of ignition sources for dusts is given in this section. A further discussion is given in Section 17.46.

17.45.1 Flames and direct heat

Incident statistics show that a large proportion of dust ignitions are caused by flames. A flame is a very effective source of ignition for dust suspensions.

One source of flames is direct fired equipment. This source may be eliminated by the use of indirect heating using hot water or steam. If this course is adopted, the basis of safety should not be negated by any additional means of heating provided as a standby.

17.45.2 Hot work

Another principal ignition source for dusts is hot work such as welding and cutting. Again a welding flame is a very effective source of ignition.

In this case it is frequently a dust layer inside equipment which is ignited. Such a dust layer may have an ignition temperature in the range 100–200°C and is readily ignited by hot work. Incidents occur because this hazard is not appreciated and the dust is not cleaned out of the equipment before work is started.

17.45.3 Incandescent material

Burning dust, or other incandescent material, is another important ignition source. Considerable efforts are made to prevent ignition by burning dust.

Burning dust is an ignition source which can occur inside dust-handling equipment. One consequence of this is that it may travel through the plant. Another is that it may remain undetected.

A direct firing system is one potential source of incandescent particles. In direct-fired driers the air inlet

is protected by a fine screen to prevent ingress of such incandescent material.

17.45.4 Hot surfaces

Hot surfaces are another important ignition source. One type of hot surface is equipment with a hot surface such as a steam pipe or electric lamp. Another is overheated moving equipment such as a distressed bearing.

Ignition due to a hot surface is particularly likely to occur with dust layers. As already mentioned, the surface temperature which can cause ignition of a dust layer is frequently no more than 100–200°C. The ignition temperature of a dust layer decreases as the thickness of the layer increases. It is frequently found in investigations of ignition that a dust layer has ignited at an unexpectedly low temperature.

Bowes and Townshend (1962) have applied self-heating theory to the prediction of the temperature at which a dust layer is liable to ignite.

Practical considerations should also be borne in mind. For example, contamination with oil may effect an appreciable reduction in the ignition temperature of a dust layer. Another factor which may lead to a lower ignition temperature is thermal degradation of the material.

The dust itself may contribute to its own ignition. Dust is a poor conductor of heat and a layer of dust on equipment may reduce heat loss to atmosphere and thus cause the surface to be hotter than it would be otherwise. Or again, dust may enter a bearing and cause it to run hot.

Hot surface ignition is a particular problem with driers of various types. A discussion of the problem with different types of drier is given by Field (1982) and detailed guidance is given in the IChemE *Drier Guide* (Reay, 1977; Abbott, 1990). Field summarizes the general recommendations of the latter as to the effect that inlet temperatures should be at least 50°C below the minimum ignition temperature of the dust suspension and 20°C below that of any dust layer likely to occur.

Electric lamps give hot surfaces which may ignite dust suspensions. There are available lamps with special protection for use in dusty atmospheres. Alternatively, areas which may contain dust suspensions, may be illuminated by lamps which are separated on the other side of an armoured glass panel.

A number of incidents have occurred, particularly in silos, involving the use of wander lamps supplied by the mains. These should be avoided and portable battery lamps used instead.

Hot surfaces may also occur as a result of distress in machinery such as pumps and motors. It may be necessary in some cases to monitor features such as bearing temperatures.

17.45.5 Electrostatic sparks

As stated in Chapter 16, there are three main types of spark which may serve as an ignition source; (1) electrostatic sparks, (2) electrical sparks and (3) friction/impact sparks. Both of the first two involve an electrical discharge, but the difference is that the first is a capacitive or inductive discharge spark and the second a spark from a voltage source.

The standard minimum ignition energy tests use an electrostatic ignition source and are therefore most directly applicable to electrostatic spark ignition, but less so to electrical sparks.

An electrostatic spark may occur due to a discharge from electrical equipment. Protection against such discharges is based on hazardous area classification and the associated safeguarding of electrical equipment. Intrinsically safe equipment is designed so that incendive capacitative or inductive discharges cannot occur.

17.45.6 Electrical sparks

Electrical sparks occur in the normal operation of certain equipment such as switches and relays and may occur in electrical equipment generally as a result of malfunction.

Again, protection against electrical sparks is based on hazardous area classification and safeguarding. In particular, flameproof equipment is used. Where dust is present this equipment should exclude dusts. A distinction may be drawn between equipment which is dust tight and excludes dust entirely and equipment which is dustproof and lets in only an insignificant amount of dust. An account of the two types of equipment is given by Field (1982).

A more detailed discussion of hazardous area classification and of safeguarding of electrical equipment, including equipment for use in dusty conditions, is given in Chapter 16.

17.45.7 Friction sparks

Another important contributor to incidents is frictional sparks associated with rubbing or grinding. These can occur in plant handling dust in several ways. The dust itself may block the equipment and cause overloading, leading to spark generation. Preventive measures include control of dust flow and machine overload trips. Foreign materials such as tramp iron can cause sparks. Removal of such objects can be effected by magnetic or pneumatic separation, and is especially desirable if the material is to pass through a mill. Failure of equipment can also give rise to sparks.

17.45.8 Impact sparks

Much concern has centred around the potential of hand tools to create an incendive impact spark, although there is little evidence from incidents of single impact ignition.

There has, however, been a good deal of work done on the potential of hand tools as an ignition source. Most of the work on this has been done on gases and an account is given in Chapter 16.

As there described, the incendive potential of an impact such as that of a metal tool on a metal surface arises from the heating of that surface. In other words, the ignition source is not the spark itself but the heated surface. The problem is the transfer of the heat from the metal surface to the dust.

Experimental work on impact ignition of dusts has been performed by Morse (n.d.), Brown (1941 BM IC 7148) and N. Gibson, Lloyd and Perry (1967). The work is summarized by Cross and Farrer (1982) to the effect that dust ignitions have been obtained either if the dust was a sensitive one such as aluminium, magnesium, zinc or sulphur, or if the thermite reaction occurred, but no ignition of a non-sensitive dust in the absence of the thermite reaction has been obtained.

17.45.9 Self-heating

An account of self-heating was given in Chapter 16, where the general features and quantitative aspects where discussed. Consideration here is limited to a few basic points.

Self-heating, or spontaneous combustion, is another significant ignition source.

There are a wide variety of reactions which can give rise to self-heating. They include not only oxidation reactions but reactions with water or wood. For many reactions the reaction rate accelerates with temperature, according to the Arrhenius equation. But there are also autocatalytic reactions which may accelerate due to production of a catalyst or removal of an inhibitor. Induction times may be long and the self-heating may be slow to start but may then proceed undetected for a long period. Account should also be taken of the effect of contaminants such as oil and of thermal degradation. It follows that the first step is screening of the dust to determine whether it is liable to self-heating.

Control of the temperature of dust in process and in storage is another means of preventing self-heating. One aspect of this is control of hot surfaces, which may arise in normal operation or due to fault conditions.

In general, situations in which there is a large mass of dust stored at a high initial temperature tend to present the greatest hazard. Dust in a pile has a high surface area and sufficient air circulation, both of which favour self-heating.

Measures should be taken to avoid unintended accumulation of deposits of dust which could undergo self-heating.

A situation which has frequently led to trouble is the discharge of hot dust from a drier into a hopper. It may be necessary to cool the dust prior to storage. Another measure which is sometimes used is to recirculate dust from storage through a cooling system.

Another precaution which is taken is the monitoring of the temperature of dust in storage.

17.45.10 Static electricity

Static electricity is a further significant ignition source for dusts. This too has been treated in Chapter 16 so that again consideration here is limited to a few basics. A more detailed discussion is given by Cross and Farrer (1982).

In general terms, the static charge on dusts is a function of the work done on them. Hence the charge tends to be a stronger function of the process than of the material. This is illustrated by the data on charges for different dust-handling processes given in Chapter 16. For sieving and pouring the charges are low, but for size reduction they are much higher.

It is not easy to screen for situations where static electricity might present a hazard in dust handling. Laboratory tests for this are not well developed.

There are certain types of dust-handling plant in which static electricity is readily generated. These include mills, conveyor belts and pneumatic conveying systems. The hazard in such equipment should therefore be carefully considered.

As with liquids, static charge can accumulate at the centre of a large storage hopper. it may then be discharged by an earthed probe. But there is also a hazard unique to dusts, that of sliding of highly charged material towards an earthed container wall.

Plastic surfaces such as those used in chutes may give rise to sparks. Bags used for transporting dusts can also create sparks. A detailed discussion of these is given by Cross and Farrer.

An operation which has resulted in a number of incidents is the pouring of powder from a polyethylene bag into a flammable solvent.

The human body can carry a charge sufficient to make it a potential ignition source. In the manual handling of dusts, the hazard of static electricity from the human body becomes significant if the dust has a minimum ignition energy less than 25 mJ.

Factors which tend to reduce the hazard of dust explosions from static electricity are the relatively high minimum ignition energy of dusts and the tendency of dusts to give corona discharge.

Measures to counter static electricity include modification of the processing conditions and of the plant. The reduction of static electricity by controlling the atmosphere at a higher relative humidity is particularly relevant to handling dusts.

In storage bins use may be made of earthed wire meshes on the wall and of earthed rods in the bulk powder. These do, however, have the disadvantage that if they lose their connection to earth, they may aggravate the situation. Another measure which is particularly relevant to storage bins is the use of passive dischargers on the material entering.

As far as the human body is concerned, the main precaution is the use of conducting footwear or antistatic footwear and conductive flooring.

If the minimum ignition energy is less than 10 mJ, it is advisable to provide antistatic flooring and to use antistatic clothing and footwear.

17.45.11 Ignition incidents

Some information on ignition sources in dust explosion incidents is given in Table 17.67. Apart from the usual problem of consistency of classification, the data show that different studies tend to highlight different ignition sources. For example, the proportion of incidents attributed to welding and cutting in the three sections of the table is 10, 3 and 24.3%, respectively.

Another important point which is illustrated particularly by section C of the table is the multiplicity of situations which can give rise to ignition. This reinforces the point often made that it is prudent to assume that the necessary attempt to eliminate all ignition sources may not be completely successful.

Further statistical data on ignition sources for dust explosions are given by Lunn (1992), as mentioned in Section 17.43. The HSE survey for 1979–88 gives for the principal ignition sources friction/mechanical failure, overheating/spontaneous heating, flames/flaming material, tramp material, welding/cutting with 56 (18%), 51 (17%), 44 (15%), 21 (7%) and 20 (7%) events, respectively; 83 (27%) events were classified in the category ‘unknown’. In the BIA survey, the main ignition sources were mechanical sparks, smouldering clumps, mechanical heating and electrostatic discharge, with 26.1%, 11.3%, 8.9% and 8.7%, respectively; 16% of events were classified in the category ‘unknown’.

Table 17.67 *Ignition sources for dust explosions*

A Ignition sources for primary dust explosions[a]

Ignition source	*Proportion* (%)
Welding and cutting	10
Friction in bucket elevator	8.5
Fire (other than welding)	7.8
Electrical	4.3
Lightning	2.8
Motors	2.1
Static electricity, foreign material, spontaneous heating, other	4.5
Unknown	60

B Ignition sources for dust explosions[b]

Ignition source	*All dusts* 1860–1957		*Grain elevators* 1958–75		*Feed mills* 1958–75		*Total* No.	(%)
	No.	(%)	No.	(%)	No.	(%)		
Foreign material	209	18.66	–	–	16	32.00	225	17.22
Fire or flame	179	15.98	11	8.03	6	12.00	196	15.00
Friction	157	14.02	12	8.76	2	4.00	171	13.08
Hot sparks, overheating	78	6.96	–	–	–	–	78	5.97
Electrical equipment	54	4.82	9	6.57	2	4.00	65	4.97
Welding and cutting	20	1.79	14	10.22	6	12.00	40	3.03
Static electricity	25	2.23	–	–	–	–	25	1.91
Spontaneous combustion	16	1.43	2	1.46	1	2.00	19	1.45
Lightning	4	0.36	4	2.92	–	–	8	0.61
Unknown	378	33.75	85	62.04	17	34.00	480	36.73
Total	1120	100	137	100	50	100	1307	100

C Probable ignition sources in elevator incidents[c]

Ignition source	*Number*	*Proportion* (%)
Welding and cutting	16	24.3
Hot bearings	7	10.6
Tramp metal	6	9.1
Electrical	4	6.0
Explosive vapour	2	3.1
Heating system	2	3.1
Dust system	2	3.1
Lightning	1	1.5
Static electricity	1	1.5
Blockage in leg	1	1.5
Extraction of oil from corncake	1	1.5
Switch engine on rail dump	1	1.5
Choked leg	1	1.5
Electrical cord in leg	1	1.5
Volatile solvent escaped from processing of soybeans	1	1.5
Grain hung up in drier	1	1.5
Fan blade caused spark	1	1.5
Unknown	17	25.7
Total	66	100

[a] After Spiegelman (1981).
[b] K.N. Palmer (1981a) after Jacobsen (1981). Original sources: NFPA (1957) for all dusts; Verkade and Chiotti (1978b) for grain elevators and mills.
[c] After Cross and Farrer (1982). Original source: Department of Agriculture (1980).

17.46 Dust Explosion Prevention

As for flammable gases, control of dust explosions may be approached by way of prevention or protection.

Accounts of dust explosion prevention include those given in *Dust Explosions in Factories* (HSE, 1970 HSW Bklt 22) (the HSE *Dust Explosion Guide*), *Guide to Dust Explosion Prevention and Protection*. Part 2: *Ignition Prevention, Containment, Inerting, Suppression and Isolation* by Schofield and Abbott for the IChemE (1988/30) (the IChemE *Dust Explosion Protection Guide*), FPA FS 6022: 1989 *Explosible Dusts: Control of Explosions*, FS 6023: 1989 Explosible Dusts: *Elimination of Ignition Sources* and NFPA 69: 1992 *Explosion Prevention Systems* and by K.N. Palmer (1973a), Bartknecht (1981a, 1989) and Eckhoff (1991).

There are several approaches to the prevention of dust explosions. They include (1) use of a dust-free process, (2) avoidance of flammable dust suspensions, (3) elimination of sources of ignition and (4) inerting.

17.46.1 Dust-free processes

A fundamental solution to the dust explosion problem is to use a dust-free process. In particular, it may be possible to process the materials wet rather than dry, so that dust suspensions do not occur at all. This approach is in effect an application of the principle of inherently safer design. Where it is applicable, it is one of the most satisfactory methods.

17.46.2 Dust control

If flammable dust has to be handled dry, it is generally not possible to prevent the occurrence of dust concentrations above the lower explosive concentration in some parts of the plant. Nevertheless, much can be done to minimize the volume of any dust clouds formed and to reduce the probability of formation.

Where dust suspensions may occur, large volumes should be avoided as far as practicable. Often it may be appropriate to have several smaller volumes rather than one large one. Overdesign of a unit, such as a hopper, should be avoided so that it does not operate empty all the time.

Situations should be avoided which encourage dust cloud formation such as the free fall of dust from a height into a hopper.

Dust should be removed from suspension at as early a stage as process considerations permit. Thus, if dust has to be removed from a gas stream, it is better to do this as soon as practicable as the gas leaves the plant rather than to transfer it down long ducts to a central cleaning point.

Buildings which contain plant handling flammable dusts should be designed to minimize the accumulation of dust deposits and to facilitate cleaning.

Avoidance of dust suspensions depends as much on operation as on design. Dusts should not be allowed to accumulate at the gas cleaning plant, but should be removed regularly in accordance with the design. Buildings which have plant handling dust should be cleaned to prevent accumulation of dust deposits.

It should be borne in mind that even if a dust suspension within the explosive range is not present in normal operation, it may be so during start-up, shutdown or fault conditions.

17.46.3 Control of ignition sources

Measures should be taken to eliminate ignition sources which could give rise to a dust explosion.

Control of ignition sources needs to be addressed both in the design and operation of the plant. Measures which can be taken in design include the location or elimination of direct firing and the avoidance of situations where static electricity can give rise to incendive sparks.

Measures to ensure close control of operations is particularly necessary for activities such as welding and cutting. Training to ensure that personnel understand the reasons for the precautions is an integral part of this.

Good housekeeping, and particularly avoidance of accumulation of dust deposits, has a role to play which is especially important in plants handling dusts.

Hazardous area classification provides a formal framework for the control of ignition sources. An account of hazardous area classification, including that for areas where combustible dusts may occur, was given in Chapter 16. Two points made there merit repetition. First, although hazardous area classification was originally concerned primarily with ignition by electrical sources, it has developed into a comprehensive system for the control of all ignition sources which might ignite a release outside the plant. Second, the effectiveness of hazardous area classification depends as much on operation as on design.

However, hazardous area classification is concerned essentially with releases from plant rather than with ignition within plant. Dusts particularly are prone to ignition from ignition sources within the plant. It is necessary, therefore, to complement the measures taken by hazardous area classification with other measures to eliminate in-plant ignition sources.

Maintenance of equipment to minimize the fault conditions which could constitute ignition sources is another significant aspect of control of ignition sources not only outside but inside equipment.

The IChemE *Guide* gives detailed measures for the control of ignition sources covering the following operations/equipment: (1) size reduction, (2) pneumatic conveying, (3) screw conveyors, (4) drag link and mass conveyors, (5) belt conveyors, (6) bucket elevators, (7) storage bins and silos and (8) dust filters.

It is generally imprudent, however, to assume that an ignition source will not occur.

17.46.4 Inerting

The suspension of a flammable dust in air may be rendered non-explosive by the addition of inert gas.

Guidance on inerting of dust-handling plant is given in the NFPA 69 and the IChemE *Guide*.

The main gases used for inerting of dust-handling plant are nitrogen, carbon dioxide, flue gas and inert gas from a generator. The IChemE *Guide* gives guidance on the factors governing selection of a suitable gas.

One factor is any hazards associated with the use of the gas. One such hazard is reaction with the dust: carbon dioxide can react violently with aluminium dust, and nitrogen can react at high temperature with magnesium dust. Carbon dioxide can also generate static electricity, as described in Chapter 16.

Other relevant factors are the availability and cost of supply.

In using inerting, complete replacement of oxygen by inert gas may be uneconomic. An alternative approach in such cases is to keep the oxygen content well below the maximum permissible oxygen concentration to prevent ignition. This concentration is obtained using the test referred to earlier.

The IChemE *Guide* also cites certain rules-of-thumb relating the maximum permissible oxygen concentration for carbon dioxide C_o and that for nitrogen N_o:

$$N_o = C_o - 2$$

$$= 1.3C_o - 6.3$$

These rules are attributed to Germany and NFPA 69: 1978, respectively.

The maximum permissible oxygen concentrations to prevent ignition which are reported in the literature are normally measured at ambient temperature. If it is proposed to use inerting for dust at high temperatures (say $> 100^\circ C$), the maximum permissible oxygen concentration to prevent ignition should be determined by tests. Likewise tests are called for if there is a hybrid vapour–dust mixture.

With regard to the safety margin to be employed, the IChemE *Guide* suggests a minimum margin of 2%. Thus if the maximum permissible oxygen concentration to prevent ignition is 11%, the oxygen concentration should be kept below 9%. It also recommends a larger margin where there are large plant volumes, extended hot surfaces or high explosibility dusts (St 3).

There will be a certain out-leak of inert gas from the plant and a certain in-leak of air, and this needs to be taken into account, by design measures to minimize these leaks and by monitoring the oxygen concentration.

Often the plant is totally enclosed and dust is added and removed through valves which give only a small loss of inert gas. Inert gas is supplied to make up these losses. Where the inert gas is recycled through the plant, it is important to avoid the accumulation in the gas of fine particles which are not removed by gas cleaning equipment and which constitute a much increased hazard if ignition occurs.

Careful design and testing of the plant is necessary to ensure that the concentration of oxygen is below the maximum permissible oxygen concentration throughout. Dead spots where there is no gas circulation should be eliminated, and low pressure points where air could leak in should be checked. Usually it is necessary to distribute the inert gas to a number of different points on the plant.

The inert gas demand is liable to vary due to causes such as material flows in the plant, materials withdrawal, temperature changes and leaks. The supply of inert gas should be sufficient to meet peak demands. It should also be reliable.

The gas should be free of moisture, rust and noxious gases. There should be controls to ensure a balanced supply to the different parts of the plant. There should be non-return valves to prevent the entry of dust into the inert gas system. It is usual to provide means of cleaning inert gas leaving the plant.

There should be continuous monitoring of the oxygen content of the gas in the plant and a trip system to shut the plant down if the concentration rises towards a hazardous level. Since the gas contains dust, there may be problems in the measurement of the oxygen level.

The inerting solution is particularly useful in handling dusts of very high explosibility ($K_{st} > 600\,bar/s$).

Inerting is not necessarily effective in eliminating dust fires.

The IChemE *Guide* gives examples of the application of inerting to grinding and spray drying operations.

It is also possible with dust suspensions to use inert dust to effect inerting. This method is utilized in certain specialized applications, of which the principal example is coal mining. Thus in the UK, limestone dust is used on the floor of mine roadways to prevent a coal dust explosion propagating. The use of inert diluent dusts is discussed in the IChemE *Guide*. The proportions of inert dust quoted as necessary to provide effective inerting are high, generally more than 60%.

Inerting may be used in combination with dust explosion suppression or venting. This is an approach which may be considered where complete elimination of combustion by inerting is judged uneconomic. In such circumstances the effect of partial inerting is to reduce the strength of the explosion to be handled by the suppression or venting system.

17.47 Dust Explosion Protection

Accounts of dust explosion protection include those given in FS 6015: 1974 *Explosible Dusts, Flammable Liquids and Gases: Explosion Suppression*, the HSE *Dust Explosion Guide* (1970 HSW Bklt 22), *Explosions* (Bartknecht, 1981a), the IChemE *Dust Explosion Protection Guide* (1988/30), *Dust Explosions* (Bartknecht, 1989), FPA FS 6022: 1989 *Explosible Dusts: Control of Explosions*, *Dust Explosions in the Process Industries* (Eckhoff, 1991) and NFPA 69: 1992 *Explosion Prevention Systems* and by K.N. Palmer (1973a), P.E. Moore (1979b, 1981, 1982b, 1984, 1986, 1990), J. Singh (1979a), Maisey (1980), Kirby (1985a), Kirby and Siwek (1986), P.E. Moore and Bartknecht (1986), Chatrathi (1992b,c) and P.E. Moore and Cooper (1993).

A relevant standard is BS 6713: 1986– *Explosion Protection Systems*.

Methods of protection against dust explosions include (1) explosion containment, (2) explosion isolation, (3) explosion suppression and (4) explosion venting. The first three methods are considered in this section and the fourth in the following section.

17.47.1 Explosion containment

The first option for dealing with a dust explosion is total containment.

A general discussion of pressure containment as opposed to pressure relief has been given by Wilday (1991), as described in Chapter 12. Accounts of the containment method for dust explosions include those given in the IChemE *Guide* and by Bartknecht (1981a), Kirby (1985) and Kirby and Siwek (1986).

In some ways containment is an attractive option, since it is an essentially passive method and avoids the problem of relief disposal. It is not usually practicable, however, to design the whole of a dust-handling plant so that it can withstand the pressures generated by dust explosions. This is particularly the case with large plants. Normally it is preferable to use some other method of

protection. Containment may be practicable, however, on small scale units and on particular equipments. Thus a grinding mill, for example, may be made strong enough to withstand a dust explosion.

The maximum explosion pressure for most flammable gases and dusts is given by Bartknecht (1981a) as about 7 barg. The IChemE *Guide* quotes for dusts the range 7–10 barg.

The static pressure is not, however, the sole criterion. The rate of pressure rise in a dust explosion is high, and the vessel must be able to withstand this dynamic loading.

The IChemE *Guide* distinguishes two basic options for containment: 'pressure resistance' and 'pressure shock resistance'. In the first the vessel is designed to withstand the explosion without deformation, whilst in the second some deformation is allowed provided the explosion is contained. If using this latter method an explosion occurs which is sufficiently severe, it may not be possible to reuse the vessel, but experience shows that generally the vessels are reusable, presumably because the explosions are not especially severe.

The use of containment raises the issue of its coverage within pressure vessel codes. Companies using the technique have tended to develop their own codes. In the UK the matter has been considered by the BSI Pressure Vessel Technical Committee (PVTC) (BSI, 1986). The IChemE *Guide* summarizes its findings to the effect that a vessel designed to BS 5500 should have sufficient reserve of strength to withstand quite rapid rates of pressure rise up to the design pressure on a one-off basis.

There are a number of engineering issues involved in the use of pressure vessels for containment of dust explosions. They include pressure piling and modes of failure, including brittle fracture. Such design is therefore a specialist matter.

One basic principle is to use rotational symmetry and to avoid large flat surfaces and angular parts.

In designing to contain a dust explosion, particular attention should be paid to the points at which dust is fed or withdrawn from the plant and to connections between units.

An alternative to full containment is partial containment. This involves the use of a stronger vessel combined with explosion relief.

17.47.2 Explosion isolation

Another option for dealing with a dust explosion is isolation.

The three basic methods of isolation are (1) automatic isolation, (2) automatic explosion suppression and (3) material chokes.

Taking these in turn, automatic isolation is applied to a pipe and involves the use of a quick acting shut-off valve. The general arrangement is similar to that used for flammable gases, as described in Section 17.11.

Details of this type of explosion isolation are given in the IChemE *Guide*. Detection of the explosion is by means of pressure and/or optical sensors. The former are usually preferred, since an optical detector can be blinded. On the other hand, a pressure sensor may not detect a weak pressure wave. A common threshold pressure setting is 0.1 bar.

Typically the quick acting isolation valve is located about 5–10 m along the pipe from the detectors and has a closure time of some 25 ms.

Bartknecht (1981a) states that rapid action barrier devices can be used to protect against explosions of dust and of hybrid dust–gas mixtures, but that for dusts rapid action slide valves are preferable to rapid action valves with moving parts in the cross-section of the pipe.

The second type of isolation is automatic explosion suppression applied to a pipe. Again the general arrangement is similar to that used for flammable gases, as described in Section 17.11.

The explosion is detected by instrumentation similar to that just described for automatic isolation. The suppressant barrier is located some 5–10 m from the detectors.

Quick acting valves operate most effectively on pipes up to about 0.5 m in diameter. Suppressant barriers have been found effective in pipes up to 2.5 m in diameter.

With both techniques the pipe should be designed to withstand the local pressure, given in the *Guide* as up to 10 barg.

The third type of isolation is the use of a material choke. This is applicable where it is necessary to have a flow of dust between units. A treatment of this method is given in the HSE *Dust Explosion Guide*.

Two commonly used types are rotary valves and worm conveyors, as shown in Figure 17.118. A variety of other types are illustrated in FS 6022.

A rotary valve, which is installed vertically and is driven by a motor, is generally designed to act as a dust explosion choke even in the absence of a head of dust above it.

There have not been many tests of the effectiveness of rotary valves as dust explosion chokes. It has been found, however, in one test, with an explosion above the valve, that the explosion was transmitted by the valve

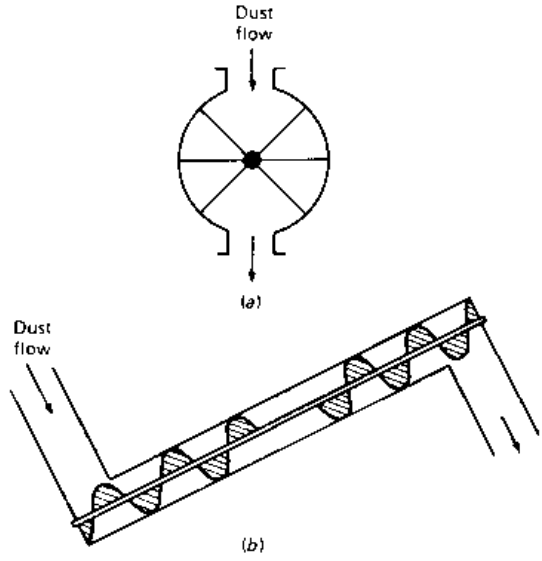


Figure 17.118 *Chokes for the isolation of sections of dust-handling plant: (a) rotary valve; (b) worm conveyor*

unless arrangements were made to trip the motor within 0.5 s of the detection of the explosion.

If a rotary valve is installed on the inlet of a hopper, there should be arrangements to prevent it from continuing to turn if the hopper becomes overfilled, since this could cause ignition by overheating the dust or overloading the motor.

A worm conveyor, which may be installed horizontally, vertically or inclined and is driven by a motor, is an alternative type of dust explosion choke. One turn of the helix is removed to prevent the choke emptying if the feed is interrupted. If the conveyor is mounted horizontally, a baffle plate is also necessary.

The motor on a worm conveyor is rather liable to be overloaded and should be provided with an overload trip. A worm conveyor is not suitable for dusts which flow less freely when heated.

Again there have been few tests on the effectiveness of worm conveyors. Since the residence time in a worm conveyor is much longer than that in a rotary valve, the former may be expected to be more effective as a dust explosion choke, but smouldering dust could still pass through unless the motor is tripped.

The choke should prevent the passage of the dust explosion and of any burning material. There should be arrangements to trip the motor. Depending on the application it may be appropriate to provide inerting or suppression.

17.47.3 Explosion suppression

Explosion suppression is the third option. Its application to explosion isolation in a pipe has been described above. Here consideration is given to its use against explosion in vessels.

Accounts of explosion suppression include those given in FS 6015 and the IChemE *Guide* and by P.E. Moore (1979b, 1981, 1982b, 1984, 1986, 1990), Bartknecht (1981a), P.E. Moore and Bartknecht (1986), Chatrathi (1992) and P.E. Moore and Cooper (1993).

Also relevant is BS 6713: 1986 *Explosion Protection Systems*. Part 4: *Method for Determination of Efficacy of Explosion Protection Systems*.

The general principle is similar to that for suppression of explosions of flammable gases, described in Section 17.11. Most published work on explosion suppression refers, however, to dusts, and a fuller account is given at this point.

Design of an explosion suppression system is based on the maximum rate of pressure rise in the explosion. This parameter has been discussed in detail in Section 17.44. It may be characterized in terms of the dust St class. In applying the basic data, account should be taken of the features of the particular application, in the light of knowledge of the factors which influence the violence of such an explosion. These include the initial pressure and turbulence and the vessel aspect ratio.

Explosion suppression requires the use of a control system, which has several functions. These are (1) to detect the explosion and inject suppressant, (2) to shut down the plant and (3) to prevent restart of the plant unless it is safe to do so.

Detection of the explosion is generally by means of a pressure sensor. Detectors are available which are robust to most materials, to condensation and corrosion, and to shock. In some cases use is made of two detectors oriented in different planes. Activation occurs when the pressure reaches its threshold value, typically of the order of 0.05 bar. In some systems use is also made of the rate of pressure rise.

The mechanisms of suppression of the explosion are (1) quenching, (2) free radical scavenging, (3) wetting and (4) inerting. Of these the principal mechanism is quenching, or abstraction of heat. The contribution of free radical scavenging is specific to the particular explosion reaction. Wetting of unburned particles is applicable to liquid suppressants. There is also some inerting effect.

The principal suppressants used are halons, dry powders, and water. The general characteristics of these have been outlined in Chapter 16. The halons used are principally Halon 1011 (chlorobromomethane), which is effective but toxic, and the less toxic Halons 1211 and 1301. The dry powder most widely used is ammonium phosphate based.

With regard to dry powder, the point has been made earlier that it effectiveness depends on complete extinction of the flame in the initial discharge. Reignition, whether due to incomplete extinction or to hot surfaces, is therefore a potential problem characteristic of this type of suppressant.

Another issue in the selection of suppressants is contamination. With halons the problem is minimal, but with dry powders it can be significant. Water may constitute a contaminant in some cases.

The IChemE *Guide* gives guidance on selection of suppressants. The use of halons is mainly confined to dust class St 1, whilst dry powders are used for both St 1 and St 2. Water is used for hydrophilic St 1 and St 2 dusts.

The effectiveness of suppression depends in large measure on the injection system. The requirement on this is that it be capable of injecting a large quantity of suppressant in a very short time and with adequate reach to all parts of the space protected. An injection system should be capable of a high mass discharge rate, a high discharge velocity and hence good 'throw' and good angular coverage.

The response time of the sensor to the explosion depends on the size of the vessel. The explosion will propagate at the speed of sound, giving a delay, or equalization time, of the order of 4 ms/m distance between the ignition source and the detector. The response of the suppression system is very rapid. The time taken for the suppressant to reach the flame depends on the discharge velocity, which initially is of the order of 40 m/s.

Two injection devices are in common use. One is a hemispherical suppressor with chemical detonator installed inside the vessel. This type is used with a liquid suppressant, usually halon. It has a limited throw, about 2.5 m, and contains only a small quantity of suppressant. The time to complete discharge is about 10–30 ms. It is suitable for protection of smaller vessels.

The other injection device is the high discharge rate (HDR) bottle, installed on the outside of the vessel and pressurized with nitrogen at 20–100 bar. This type is much more versatile, being able to handle most common suppressants and available in capacities from 0.003 to 0.1 m^3. The time to complete discharge is about 100 ms.

The size of vessel which can be protected by suppression is limited by the factors described. Over the years various figures have been quoted for the limiting size. The figure given in FS 6016: 1974 was 115 m^3. That quoted in the IChemE *Guide* is 1000 m^3. Relevant work is described by P.E. Moore (1986).

An effective suppression system requires rapid detection, rapid injection and an adequate quantity of suppressant. The IChemE *Guide* gives a number of graphs of the course of failed suppressions which illustrate these points.

Extinction of the flame is not, however, the only requirement on the suppression system. Its other function in respect of the explosion itself is to limit the pressure developed. Factors affecting this pressure are the dust St class and the detection and injection times.

One measure which may be taken to limit the pressure is the use of multiple injection points.

BS 6713: Part 4 gives criteria to be applied in determining the safe operating regime of an explosion suppression system.

Various applications of explosion suppression are described in the IChemE *Guide*, which treats (1) mills, (2) bunkers, (3) mixers, (4) elevators and (5) spray driers.

17.48 Dust Explosion Venting

The use of explosion venting is generally an effective and economic method of providing protection against dust explosions, and is the method normally considered.

Dust explosion venting is dealt with in most of the publications referred to at the start of Section 17.43, and particularly in *Dust Explosions in Factories* (HSE, 1970 HSW Bklt 22), *Dust Explosions and Fires* (K.N. Palmer, 1973a), *Dust Explosions* (Field, 1982), *Development and Control of Dust Explosions* (Nagy and Verakis, 1983) and *Dust Explosions in the Process Industries* (Eckhoff, 1991).

The set of monographs on gas and dust explosions published by the IChemE includes the following on dust explosion venting: *A User Guide to Dust and Fume Control* by C.R. Smith (1981) with a second edition by D.M. Muir (1985) and a revised second edition by Lunn (1992a) and *Guide to Dust Explosion Prevention and Protection* (the IChemE *Dust Explosion Protection Guide*), in three parts: Part 1, *Venting* by Schofield (1984) with a second edition by Lunn (1992b) (the IChemE *Dust Explosion Venting Guide*); Part 2, *Ignition Prevention, Containment, Inerting, Suppression and Isolation* by Schofield and Abbott (1988); and Part 3, *Venting of Weak Explosions and the Effect of Vent Ducts* by Lunn (1988).

Further guidance is given in NFPA 68: 1994. Much of the literature refers to the earlier 1974 edition (reaffirmed 1978).

Venting is suitable only if there is a safe discharge for the material vented. Preferably the plant should be in the open. If it is in a building, it should be possible to effect a discharge through a short duct. Any such duct will have an effect on the maximum vented pressure and the whole problem should therefore be considered at an early stage of the design.

The venting solution is not appropriate if the plant contains toxic dusts, or other associated toxic substances, which cannot be vented to atmosphere or is awkwardly sited so that safe discharge is not possible.

17.48.1 Dust explosion venting of vessels

The venting of gas explosions was dealt with in Section 17.12. For dust explosion venting, the general approach and some of the methods are similar, but there are also some important differences.

A dust explosion can occur only if the dust is dispersed. It follows, therefore, that one of the conditions for a dust explosion is a degree of turbulence. A gas explosion on the other hand may occur with a gas mixture which is initially quiescent.

Another difference is that the dust cloud tends not to be uniform, although a high degree of turbulence tends to promote uniformity.

The comments made in Section 17.12 concerning the definitions and units used in explosion venting of gases apply equally to dust explosion venting. The definitions and units used here are summarized in the Notation.

17.48.2 Factors influencing dust explosions

An account of the factors which affect dust explosibility was given in Section 17.44. There are in addition other factors which influence the strength of an explosion of a dust of given explosibility.

The maximum explosion pressure and maximum rate of pressure rise are affected by a number of factors. These are discussed by Cross and Farrer (1982), Field (1982), and Nagy and Verakis (1983). They include

(1) vessel size and shape,
(2) dust concentration,
(3) initial pressure,
(4) initial temperature,
(5) initial turbulence,
(6) ignition source,

and the presence of

(7) flammable gas,
(8) inert gas or dust.

The maximum explosion pressure is essentially independent of vessel size provided heat effects are disregarded.

Experimental measurements of maximum explosion pressure tend to show considerable scatter. Data given by Nagy and Verakis show scatter with most points lying within the ± 15% band.

For elongated vessels the heat loss tends to be more significant and the maximum explosion pressure less.

The maximum rate of pressure rise is affected by vessel size and shape. Equation 17.7.48 shows the maximum rate of pressure rise follows the cube root law and is inversely proportional to $V^{\frac{1}{3}}$. Equation 17.7.75 shows that it is proportional to the surface area/volume ratio S/V.

The dust concentration with the highest explosibility, as measured by the characteristics described earlier such as minimum ignition temperature, minimum ignition energy and maximum rate of pressure rise, tends to be several times greater than the stoichiometric concentration. This contrasts with gas mixtures where the most explosive concentration is usually close to, though not at, the stoichiometric value. The effect of dust concentration is illustrated in Figure 17.119.

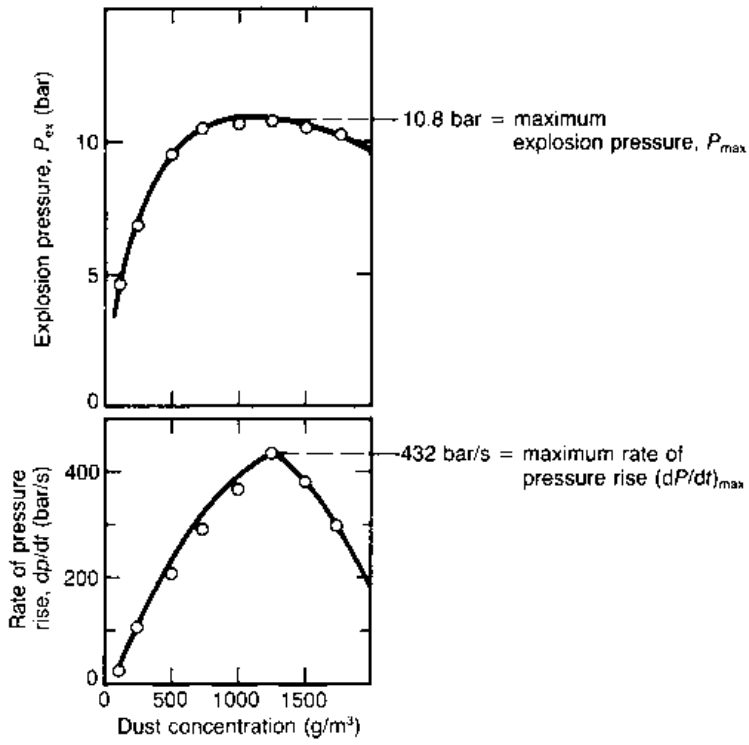


Figure 17.119 *Dust explosion pressure: effect of dust concentration (Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

There is surprisingly little information on the effect of initial pressure. One reason may be that most plant handling dusts operates close to atmospheric pressure. The account of the effect of this parameter given by Nagy and Verakis is in fact relative to gas explosions. According to Field, whereas in a gas explosion the maximum explosion pressure is proportional to the initial pressure, the effect is less for dust explosions. However, data given by Bartknecht for starch dust show maximum explosion pressure proportional to initial pressure for initial pressures up to 2 bara. The same data set show that the maximum rate of pressure rise is also proportional to initial pressure for the same range of initial pressures.

The initial temperature may have several effects. These include reduction of the mass of air available for combustion and reduction of the moisture content of the dust. The net effect of an increase in initial temperature may therefore be to reduce rather than increase the maximum explosion pressure. An increase in initial temperature does, however, increase the maximum rate of pressure rise through its effect on the combustion rate, and also through any reduction in moisture content.

As already indicated, it is difficult to envisage a dust explosion without a degree of initial turbulence. Turbulence tends, however, to be non-uniform and difficult to measure or quantify. In general terms, an increase in initial turbulence will have only a weak effect on the maximum explosion pressure, but a strong effect on the maximum rate of pressure rise. Situations associated with high turbulence include grinding operations.

The effect of the ignition source on the strength of the explosion is complex and depends essentially on the nature as well as the strength of the ignition source. This aspect was discussed in Section 17.44. In brief, some experiments have shown that similar K_{st} values are obtained for ignition by condenser discharge with an ignition energy in the range 0.005 to 8 J and by chemical detonator with an ignition energy of 10 000 J.

The effects of the presence of flammable gas and/or inert gas or inert dust have already been described in discussing dust explosibility.

17.48.3 Experimental studies

There have been a number of experimental studies of dust explosion venting of vessels. Some of the principal studies are listed in Table 17.68.

Early work on dust explosion relief was done at the Bureau of Mines by Hartmann, Cooper and Jacobsen (1950 BM RI 4725) using corn starch and by Hartmann and Nagy (1957) using cellulose acetate. According to Nagy and Verakis (1983), the Bureau of Mines has performed some 10 000 experiments on vented explosions. The principal enclosures used were 0.32, 1, 64 and 216 ft^3 in size, the first being cylindrical, the second cubical and the others rectangular galleries.

Table 17.68 *Dust explosion venting: some experimental studies*

Investigators	*Vessel or enclosure type*	*Volume*	*Dust*
Hartmann, Cooper and Jacobsen (BM 1950 RI 4275)	Galleries	1, 64, 216 ft^3	Corn starch
Hartmann and Nagy (1957)	Gallery	1 ft^3	Cellulose acetate
Schwab and Othmer (1964)	Cylindrical chamber	0.0461 ft^3	Plastics dusts, metallic stearate dusts
Donat (1971b)	Sphere	1 m^3	Coal dust, dextrin, organic pigment, aluminium dust
Eckhoff and Fuhre (1983)	Silo	500 m^3	
Eckhoff, Fuhre and Pedersen (1986, 1987); Eckhoff *et al.* 1988)	Silo	236 m^3	Maize starch
Radant (1982)	Silo	20 m^3	
Nagy and Verakis (1983)[a]	Galleries	0.32, 1, 64, 216 ft^3	Various[b]

[a] Account based essentially on earlier work at the Bureau of Mines.
[b] Dusts tested comprised some 19 dusts including atomized aluminium, cellulose acetate, chromium dust, coal dust, cornstarch, magnesium dust, wheat starch, several plastics dusts and several flours. Not all of these were tested in each chamber.

Schwab and Othmer (1964) carried out experiments using plastics and metallic stearate dusts.

Donat (1971b) has carried out experiments in 1 and 30 m^3 vessels on coal, organic pigment, dextrin and aluminium dusts.

Bartknecht (1981a) has described experiments, including those of Donat, in a 20 litre sphere and a 1 m^3 sphere on a number of parameters for a wide variety of dusts.

The HSE has carried out experiments on a 20 litre sphere and an 18.5 m^3 cylindrical vessel to investigate a number of features of venting, including extension of the K_{st} method (Lunn, Brookes and Nicol, 1988) and the effect of vent ducts (Lunn, Crowhurst and Hey, 1988).

Experimental studies of dust explosion relief of silos have been performed by Eckhoff and co-workers (e.g. Eckhoff *et al.*, 1982; Eckhoff and Fuhre, 1983; Eckhoff *et al.*, 1984; Eckhoff, Fuhre and Pedersen, 1986, 1987) and Radant (1982), as described below.

17.48.4 Empirical methods

In contrast to the situation with gas explosion venting there is a lack of empirical methods which do not rely on experimental data. This is not surprising in view of the difficulty of characterizing dust explosibility other than by test data and the complexity of dust explosions.

17.48.5 Scaling methods

The empirical approach used for dust explosions is the use of scaling laws validated over a wide range of experimental conditions.

The three scaling methods used are similar to those used for gas explosion venting: the vent ratio method, the vent coefficient method and the K_{st} method.

In dust explosion venting, the traditional approach has been to express the venting requirement as a vent area per unit volume of space protection, the vent ratio approach. This contrasts with the approach which has developed in gas explosion venting where the venting requirement is generally expressed as a vent area per unit cross-sectional area of space protected, the vent coefficient approach.

17.48.6 Vent ratio method

The vent ratio f is defined as for gas explosions as

$$f = A_v/V \qquad [17.48.1]$$

where A_v is the vent area, f is the vent ratio and V is the volume of the enclosure.

As already mentioned, a common method of characterizing the vent area required is to plot the reduced explosion pressure as a function of vent ratio. Such a plot for dusts given by Hartmann, Cooper and Jacobsen for data covering a range of volumes from 1 to 216 ft^3 is shown in Figure 17.120. Numerous other plots for dusts are given by Lunn.

Recommended values of the vent ratio have been given by various sources. Table 17.69 gives some values which have been available for some time, but which are also quoted by Lunn. Section A of the table gives values recommended for volumes up to 1000 ft^3 by K.N. Palmer (1973a) on the basis of the Hartmann bomb maximum rate of pressure rise values. Section B gives values

recommended by NFPA 68: 1978 without reference to dust explosibility measurements.

Palmer states that dusts with a very high maximum rate of pressure rise (say $>12\,000\,lb_f/in.^2\,s$) should be treated with particular caution. For these, venting may not be sufficient or even appropriate.

17.48.7 Vent coefficient method

The vent coefficient K is likewise defined as for gas explosions:

$$K = A_c/A_v \qquad [17.48.2]$$

with

$$A_c = L_1 L_2 \qquad [17.48.3]$$

where A_c is the area of the smallest cross-section of the enclosure, K is the vent coefficient and L_1 and L_2 are the two smallest dimensions of the enclosure.

N. Gibson and Harris (1976) have shown that a vent coefficient $K = 3$ gives good agreement with Donat's data for organic pigment and for St 2 dust. Their results have been given in Figure 17.24.

17.48.8 K_{st} method

The K_{st} method developed by Bartknecht is based on the cube root law given in Equation 17.44.3. The cube root law in terms of the maximum rate of pressure rise is

$$\left(\frac{dP}{dt}\right)_{max} V^{\frac{1}{3}} = K_{st} \qquad [17.48.4]$$

and in terms of the rate of pressure rise with venting

$$\left(\frac{dP}{dt}\right)_{Pred} V^{\frac{1}{3}} = K_{st} \qquad [17.48.5]$$

Thus for the same reduced pressure the vent ratio f also follows the cube root law:

$$fV^{\frac{1}{3}} = \text{constant} \qquad [17.48.6]$$

Bartknecht gives a set of nomographs for the vent area A_v where

$$A_v = f(V, K_{st}, P_{stat}, P_{red}) \qquad [17.48.7]$$

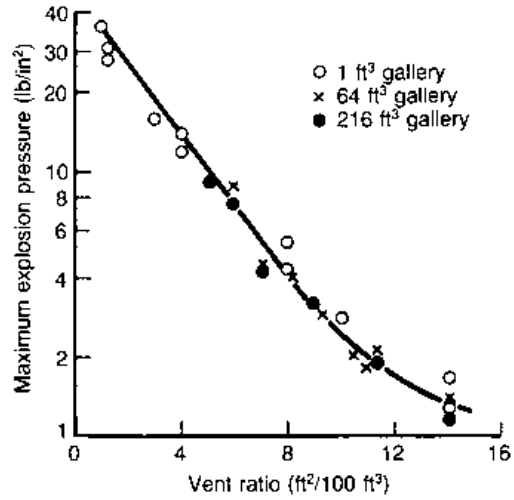


Figure 17.120 *Dust explosion venting: effect of vent ratio on reduced explosion pressure (Hartmann, Cooper and Jacobsen, 1950 BM RI 4725)*

Table 17.69 *Dust explosion venting: vent ratio recommendations*

A Smaller volumes ($\leq 1000\,ft^3$) (K.N. Palmer, 1973a)

Maximum rate of pressure rise in Hartman bomb, $(dP/dt)_{max}$ ($lbf/in.^2\,s$)	*Vent ratio* (ft^2/ft^3)
<5000	1/20
5000–10 000	1/15
>10 000	1/10

B Large volumes (NFPA 68: 1978; Lunn, 1984b)

Volume (ft^3)	*Other details*	*Vent ratio* (ft^2/ft^3)
1000–25 000	–[a]	1/30–1/50
>25 000	Small fraction obstructed, and	
	Heavy reinforced concrete construction	1/80
	Light reinforced concrete construction	1/60—1/80
	Lightweight construction	1/50—1/60
	Large fraction obstructed	1/10—1/50

[a] An attempt should be made to predict the location of the ignition source and the volume of the dust suspension.

where P_{red} is the reduced pressure and P_{stat} the vent opening pressure.

The derivation of these nomographs has been described by Lunn, Brookes and Nicol (1988). The equation from which the nomographs are derived is that of Heinrich

$$A_v = \frac{V^{\frac{2}{3}} V_L^{\frac{1}{3}} (dP_{ex}/dt)_{PredVL}}{C_d (2RT/M)^{\frac{1}{2}} P_{red}^{\frac{1}{2}} (P_{red} - P_a)^{\frac{1}{2}}} \quad [17.48.8]$$

where C_d is the coefficient of discharge, M is the molecular weight of the vented gas, P_a is the atmospheric pressure, P_{red} is the reduced pressure, $(dP_{ex}/dt)_{P_{red}VL}$ is the maximum rate of pressure rise in the test vessel, R is the universal gas constant, T is the absolute temperature of the vented gas, V is the volume of the vessel and V_L is the volume of the test vessel. The derivation of this equation is given below.

Bartknecht has given the correlations for dust explosion venting in nomograph form. His nomograph method is that adopted in VDI 3673: 1979 *The Pressure Relief of Dust Explosions*, NFPA 68 and the IChemE *Dust Explosion Venting Guide*.

The nomographs were adopted in NFPA 68: 1988, are given in the current edition NFPA 68: 1994 and are shown in Figure 17.121. The nomographs are for a high energy (10 000 J) ignition source, and there is a separate nomograph for each value of the vent opening pressure P_{stat}. The three values of P_{stat} are 0.1, 0.2 and 0.5 barg and that of P_{red} is 0.2–2.0 barg.

NFPA 68: 1978 gave two separate sets of nomographs, for strong (high energy) and weak (low energy) ignition sources. Only the first set is given in the later editions.

The nomographs apply to dusts with $K_{st} < 300$ bar m/s and with maximum explosion pressure P_{max} up to 10 barg and to dusts with $K_{st} > 300$ bar m/s and with P_{max} up to 12 barg.

The nomographs are valid within a limited range of conditions. Their use is not recommended for $V > 1000\,m^3$, $K_{st} < 50$ bar m/s and the values of P_{stat} and P_{red} just stated.

The vent area given by the nomographs for both gases and dusts in a vessel of volume 1 m^3 was given in Figure 17.22.

Bartknecht distinguishes between small and large vessels, defining the latter as $V > 30\,m^3$. He states that the nomographs tend to oversize the vent area for large volumes.

An equation equivalent to the Bartknecht nomographs shown in Figure 17.121(a)–(c) has been given by Simpson (1986) and is quoted in NFPA 68: 1994. It is

$$A_v = aV^{\frac{2}{3}} K_{st}^b P_{red}^c \quad [17.48.9]$$

with

$$a = 0.000\,571 \exp(2P_{stat}) \quad [17.48.10a]$$

$$b = 0.978 \exp(-0.105 P_{stat}) \quad [17.48.10b]$$

$$c = -0.687 \exp(0.226 P_{stat}) \quad [17.48.10c]$$

where the units are as follows: A_v (m^2), K_{st} (bar m/s), P_{red} (barg), P_{stat} (barg) and V (m^3). The range of validity of the equation is

$$1 \le V \le 1000;\ 50 \le K_{st} \le 600;\ 0.1 \le P_{stat} \le 0.5;$$

$$P_{stat} + 0.1 \le P_{red} \le 2$$

Figures 17.121(a)–(c) are given in terms of the K_{st} value. NFPA 68: 1994 also provides nomographs in terms of the st value. For the latter it gives the following equation, attributed to Schwab:

$$\log A_v + C = a \log V + \frac{b}{P_{red}^d} \quad [17.48.11]$$

with the following values of the constants:

P_{stat} (barg)	C			a	b	d
	St 1	*St 2*	*St 3*			
0.1	1.888 54	1.698 46	1.508 21	0.670 05	0.960 27	0.211 9
0.2	1.931 33	1.715 83	1.501 15	0.671 91	1.031 12	0.3
0.5	1.943 57	1.696 27	1.504 73	0.659 25	1.200 83	0.391 6

where the units are A_v (m^2), P_{red} (barg), P_{stat} (barg) and V (m^3).

Extension and extrapolation of the nomographs is discussed in NFPA 68: 1994.

The Bartknecht nomographs have been extended by Lunn, Brookes and Nicol (1988). The extrapolation is based on Equation 17.48.8. This equation does not include P_{stat} explicitly. But the experiments of Donat give values of $(dP_{ex}/dt)_{P_{red}VL}$ for the three values of P_{stat}. The authors plot $(dP_{ex}/dt)_{P_{red}VL}$ vs $(dP/dt)_{maxVL}$ for the three P_{stat} values. Then applying the cube root law (Equation 17.44.3) and taking $V_L = 1\,m^3$ yields

$$\left(\frac{dP_{ex}}{dt}\right)_{P_{red}VL} = BK_{st} \quad [17.48.12]$$

The values of B are 0.283, 0.333 and 0.5 for values of P_{stat} of 1.1, 1.2 and 1.5 bara, respectively. They take B as a function of P_{stat} so that the effect of P_{stat} enters Equation 17.48.8 via the term $(dP_{ex}/dt)_{P_{red}VL}$.

The extended nomographs given by these authors are shown in Figure 17.122. The nomographs show extension down to $K_{st} = 10$ bar m/s, $P_{stat} \le 1.1$ bara and $P_{red} = 1.02$ bara. The authors recommend that for $1.05 < P_{red} < 1.2$ the lower limit of P_{stat} be taken as $P_{stat} \le [1 + (P_{red} - 1)/2]$.

The nomographs have been validated by tests with low K_{st} dusts in a 18.5 m^3 vessel. Like the original nomographs they incorporate a safety factor. However, where the K_{st} value is low, it is important that it be determined accurately and that in using the nomograph the next highest value of K_{st} be used. The detailed limitations of the extended nomographs are discussed by the authors.

The IChemE *Dust Explosion Protection Guide* Part 3 gives detailed guidance on the application of venting to weak explosions and on the effect of vent ducts. It contains a large number of graphs for the estimation of the reduced explosion pressure in vent ducts which are straight (Appendix 1) or have a single, sharp 45° bend (Appendix 2) or a single sharp 90° bend (Appendix 3).

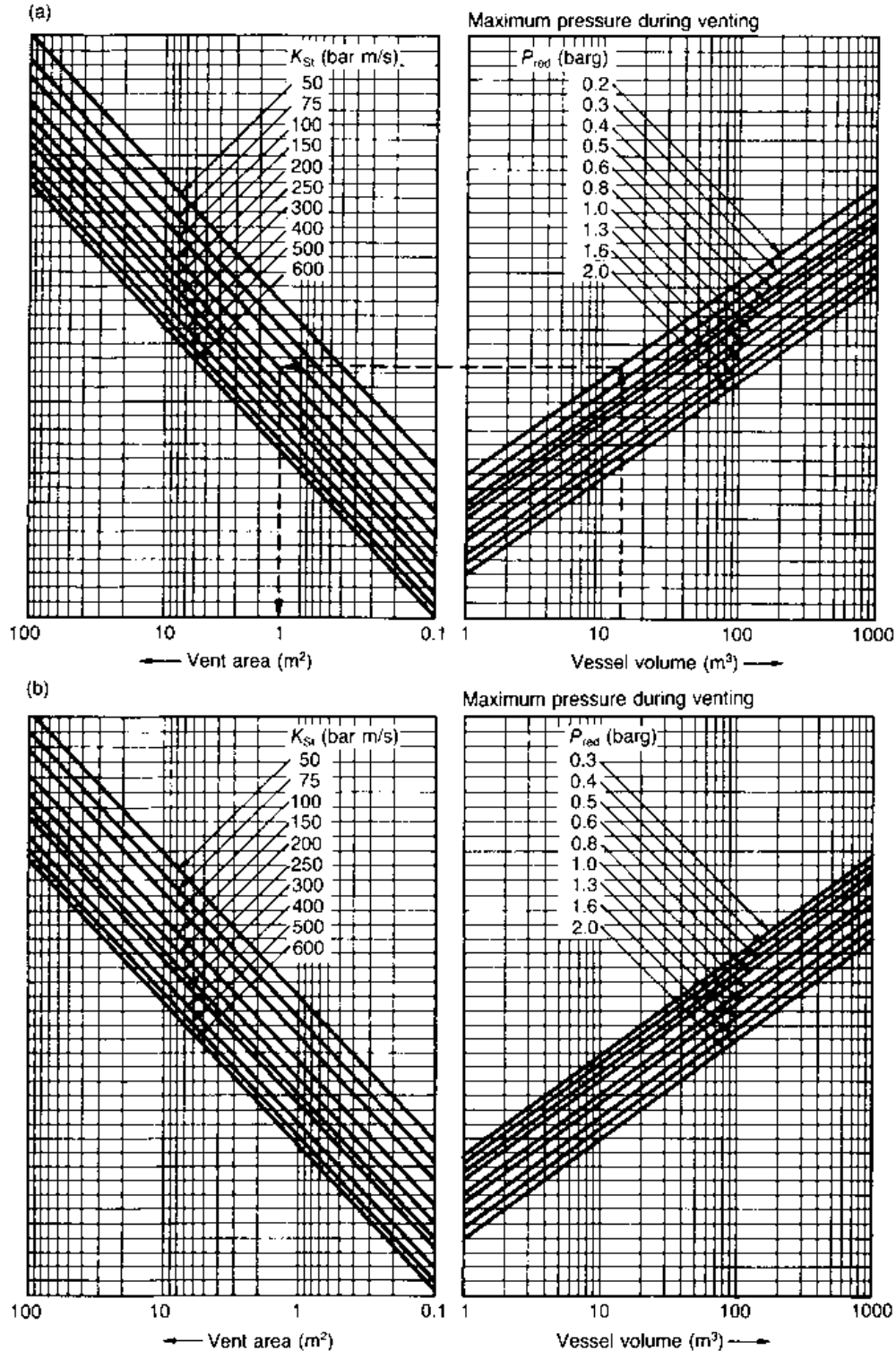


Figure 17.121 *Dust explosion venting: nomographs for vent area for high energy ignition source (NFPA 68: 1994). (a) $P_{stat} = 0.1$ barg; (b) $P_{stat} = 0.2$ barg; (c) $P_{stat} = 0.5$ barg; See text for details and note to Figure 17.25 (Reprinted with permission from NFPA 68 Deflagration Venting, copyright © 1994, National Fire Protection Association, Quincy, MA 02269).*

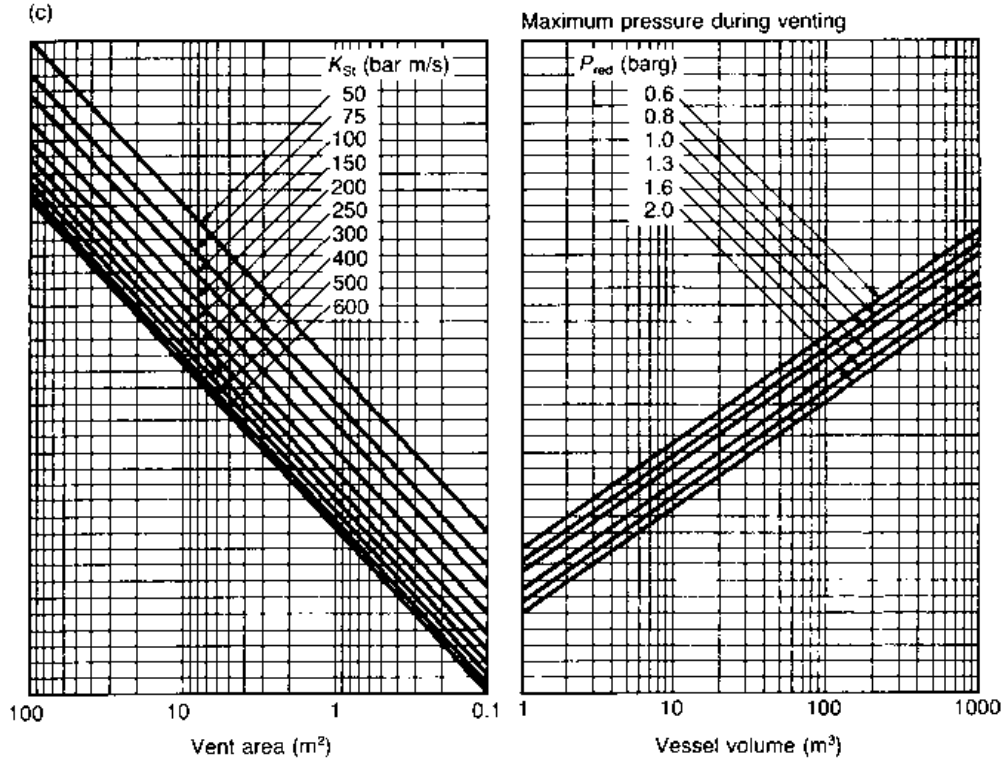


Figure 17.121 *Continued*

17.48.9 Schwab and Othmer method

Schwab and Othmer (1964) presented an empirical correlation of experimental tests performed using a Hartmann bomb type of apparatus of volume 1.3 litres. The dusts tested included powders of polymers and metal stearates.

They expressed their results in the form

$$Y = \frac{A}{10^{KX}} \qquad [17.48.13a]$$

where A is the maximum pressure in the unvented explosion (psi), X is the vent ratio ($ft^2/100\,ft^3$), Y is the reduced pressure in the vented explosion (psi) and K is the slope of the line of maximum pressure A vs vent ratio X. This is equivalent to the relationship

$$P_{red} = \frac{P_{max}}{10^{Sf'}} \qquad [17.48.13b]$$

where f' is the vent ratio, P_{red} is the reduced pressure and S is a constant.

For the rates of pressure rise, Schwab and Othmer gave the equations

$$R = \frac{5500}{10^{2.443K}} \qquad [17.48.14a]$$

$$R' = \frac{2700}{10^{2.443K}} \qquad [17.48.14b]$$

where R and R' are the maximum and average rates of pressure rise (psi/s), respectively. These equations are equivalent to

$$\left(\frac{dP}{dt}\right)_{max} = \frac{k_{max}}{10^{Kf'}} \qquad [17.48.15a]$$

$$\left(\frac{dP}{dt}\right)_{av} = \frac{k_{av}}{10^{Kf'}} \qquad [17.48.15b]$$

where $(dP/dt)_{max}$ and $(dP/dt)_{av}$ are the maximum and average rates of pressure rise, respectively, and k_{av} and k_{max} are constants.

The authors give a nomograph for the determination of the vent ratio X. This is shown in Figure 7.123.

17.48.10 Runes method

The method of Runes was described in Section 17.12. The Runes equation is

$$A_v = C\frac{A_c}{(\Delta P)^{\frac{1}{2}}} \qquad [17.48.16]$$

where ΔP is the explosion overpressure and C is the Runes constant.

NFPA 68: 1978 gives values of the Runes constant C in metric units as 6.8 for organic dusts and 10.5 for high flame speed metal dusts. These compare with values of 6.8 for propane and 10.5 for ethylene.

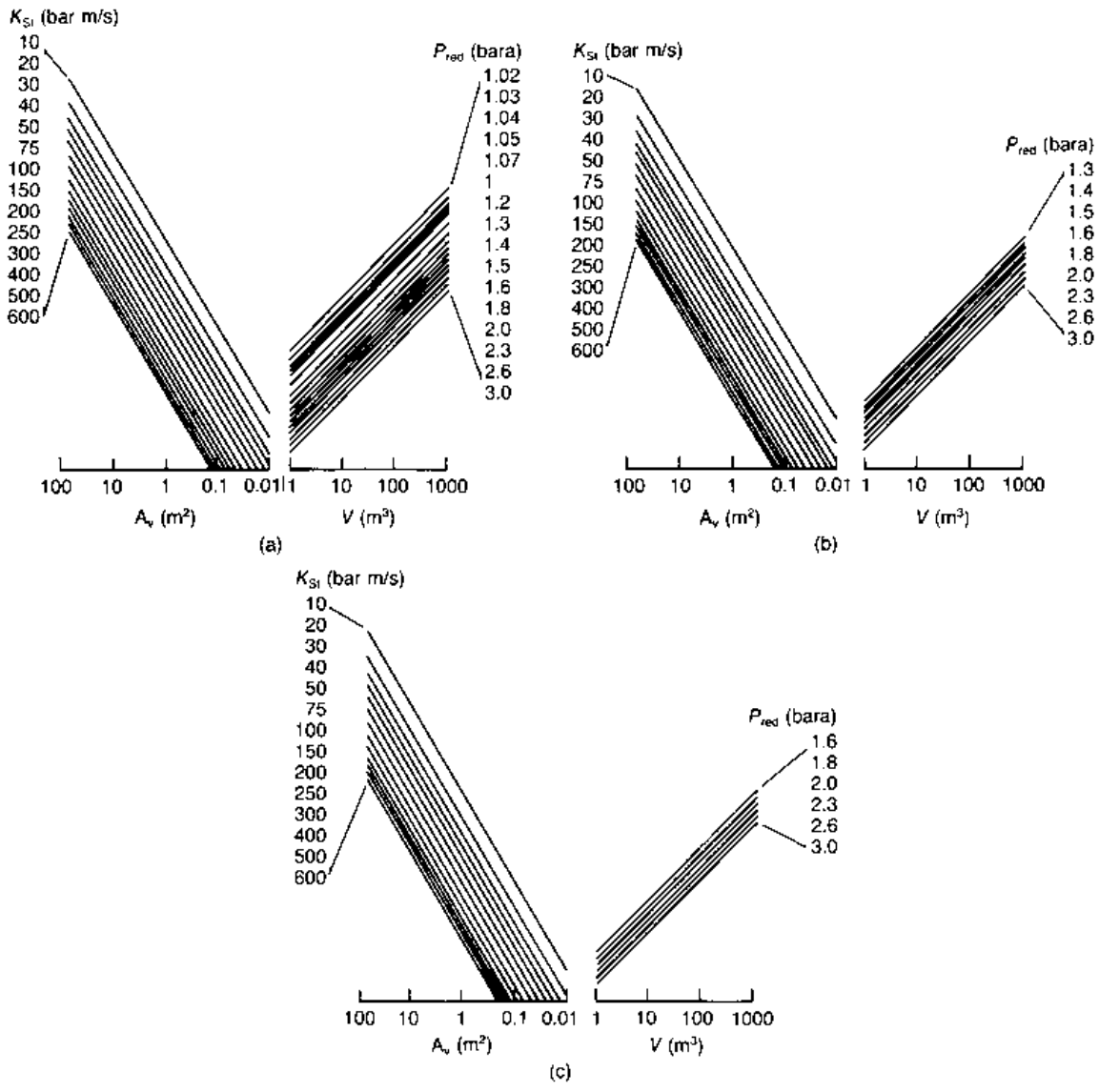


Figure 17.122 *Dust explosion venting: nomographs for vent area extended to lower reduced pressure (Lunn, Brookes and Nicol, 1988): (a) $P_{stat} \leq 1.1$ bara; (b) $P_{stat} = 1.2$ bara; (c) $P_{stat} = 1.5$ bara (Courtesy of Butterworth-Heinemann)*

NFPA 68: 1994 gives a relationship similar to Equation 17.48.16 and containing a constant C. It is described in Section 17.14. The code gives the following value of C for dusts:

Dust class	C ($bar^{1/2}$)
St 1	0.026
St 2	0.030
St 3	0.051

17.48.11 Critique of empirical methods

A review of experimental studies comparing the predictions of empirical methods with experimental results is given by Lunn.

Comparison of the empirical correlations for gas explosion venting of Cubbage and Simmonds, Rasbash, Decker, Dragosavic, Cubbage and Marshall, and Runes with the experimental work of Hartmann, Cooper and Jacobsen and of Donat, gave generally poor agreement. The Schwab and Othmer method gave excellent agreement with the results of Hartmann, Cooper and Jacob.

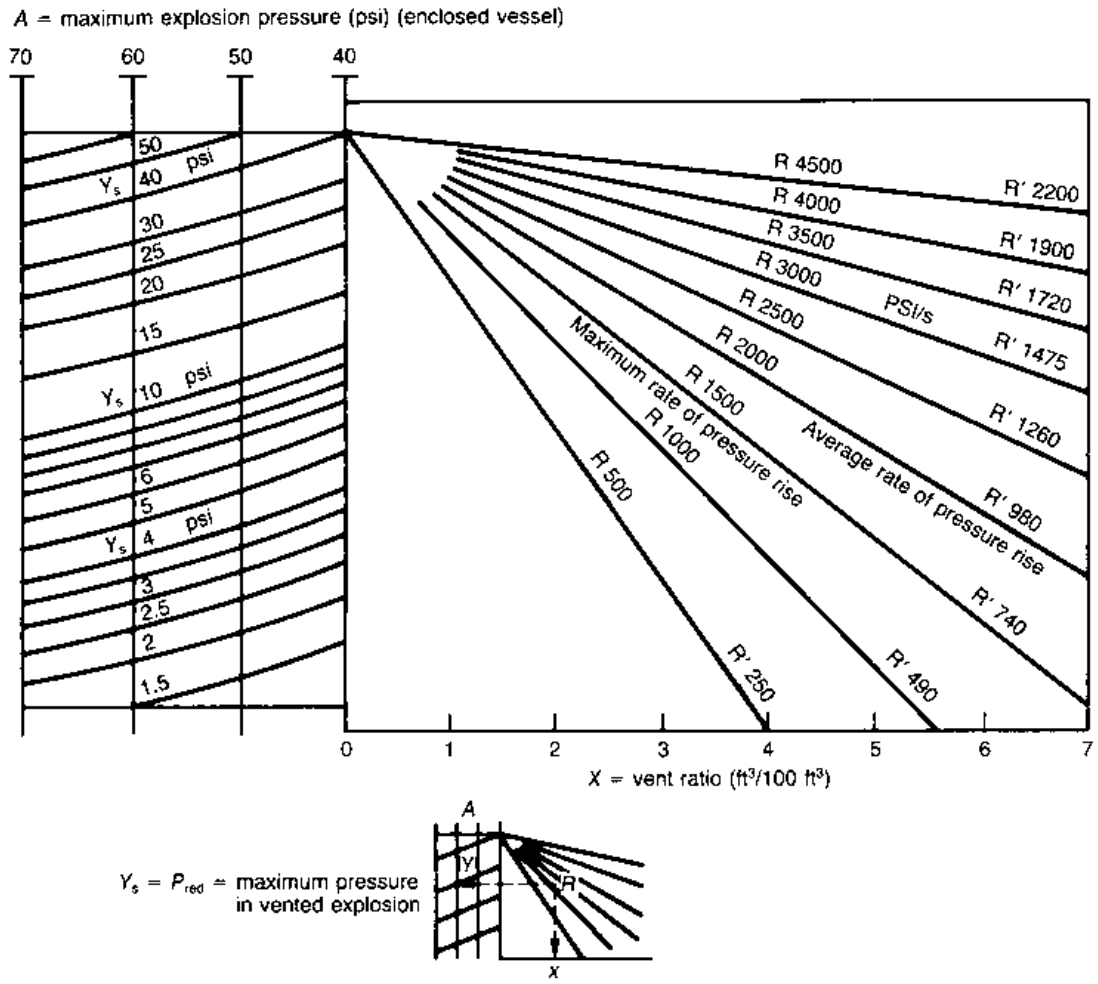


Figure 17.123 *Dust explosion venting: Schwab and Othmer nomograph for vent area (Lunn, 1984b; after Schwab and Othmer, 1964) (Courtesy of the Institution of Chemical Engineers)*

The methods considered by Lunn are primarily the vent ratio, vent coefficient and K_{st} methods and the methods of Heinrich and Rust. He gives a set of graphs comparing the predictions given by these methods with the results of Donat for 1 and 30 m^3 spheres. One of these graphs is shown in Figure 17.124. The vent coefficient and vent ratio methods were assessed by scaling up the results on the smaller vessel to the larger vessel, so that predictions were available only for the 30 m^3 vessel. The vent ratio method consistently overestimated the explosion pressure. The vent coefficient method gave closer agreement, but tended to underestimate the explosion pressure. Predictions for the K_{st} method were made for both sizes of vessel. For the 1 m^3 vessel the low ignition energy source nomographs gave good predictions for dusts in classes St 1 to 3. For the 30 m^3 vessel the low ignition energy source nomographs again gave reasonable agreement, but always tended to underestimate the explosion pressure, sometimes substantially.

Overall, Lunn recommends the use of the K_{st} method. It generally tends to overestimate the vent area and will normally give adequately sized vent areas. He points out, however, that the method can give underestimates, as shown by the work of Eckhoff on silos.

Lunn also states that if reliable Hartman bomb data are available, the Schwab and Othmer method yields good results.

17.48.12 Modelling of dust explosion venting

In principle methods developed in the modelling of gas explosion venting given in Section 17.12 may be used for dust explosion venting also, but in practice there are difficulties. These arise mainly because the models

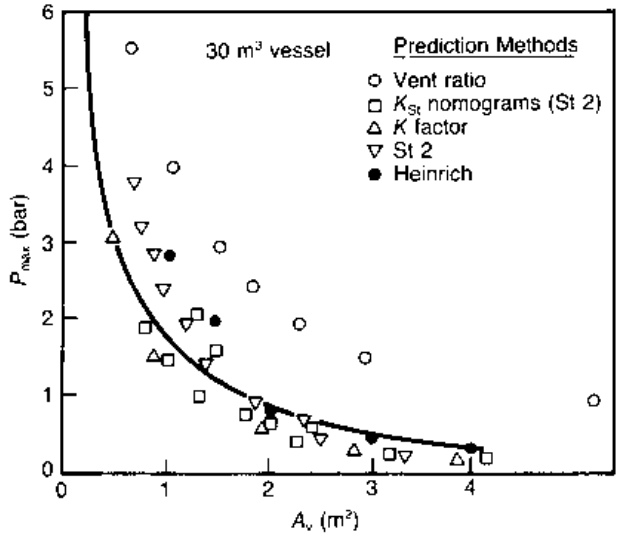


Figure 17.124 *Dust explosion venting: comparison of selected methods of vent area prediction with experimental results of Donat (Lunn, 1984b). The curve is Donat's experimental results for organic pigment in a 30 m^3 vessel (Courtesy of the Institution of Chemical Engineers)*

involve the use of the burning velocity and a turbulence factor which are difficult to specify for dust explosions. Therefore models for dust explosion venting tend to be constructed so that they can incorporate experimentally measured parameters.

17.48.13 Heinrich method

One of the first methods to use this approach was that of Heinrich (1966, 1974). The method is discussed by Matsuda and Naito (1975), Lunn (1984b) and Nicol (1988).

Heinrich made the assumption that the condition for effective relief is

$$\left(\frac{\mathrm{d}P}{\mathrm{d}t}\right)_{P_{\mathrm{red}},\,V} = \left(\frac{\mathrm{d}P_{\mathrm{ex}}}{\mathrm{d}t}\right)_{P_{\mathrm{red}},\,V} \qquad [17.48.17]$$

where P is the absolute pressure, P_{ex} is the pressure due to the explosion, t is the time and subscripts P_{red} and V refer to venting at reduced pressure and in volume V, respectively. The right-hand side of Equation 17.48.17 represents the rate of pressure increase due to the explosion, and the left-hand side represents the rate of pressure decrease due to venting. The terms are equal at $\mathrm{d}P/\mathrm{d}t = 0$ and $P = P_{red}$, where P_{red} is the absolute reduced pressure.

The rate of pressure rise in the actual vessel is related to that in a test vessel by use of the cube root law

$$\left(\frac{\mathrm{d}P_{\mathrm{ex}}}{\mathrm{d}t}\right)_{P_{\mathrm{red}},\,V} V^{\frac{1}{3}} = \left(\frac{\mathrm{d}P_{\mathrm{ex}}}{\mathrm{d}t}\right)_{P_{\mathrm{red}},\,V_{\mathrm{L}}} V_{\mathrm{L}}^{\frac{1}{3}} \qquad [17.48.18]$$

where V is the volume of the actual vessel, V_L is the volume of the test vessel and the subscript VL refers to the test vessel volume.

The volume rate of generation of burned gas is

$$\frac{V}{P}\frac{\mathrm{d}P}{\mathrm{d}t} \qquad [17.48.19]$$

and the mass rate is

$$\frac{V\rho}{P}\frac{\mathrm{d}P}{\mathrm{d}t} \qquad [17.48.20]$$

where ρ is the density of the mixture.

The mass velocity of vent outflow for the isothermal case is given by Equation 17.12.62. Then equating the mass rate of generation of burned gas given by Equation 17.48.20 to the mass vent outflow obtained from Equation 17.12.62 and utilizing Equation 17.48.18 gives for the vent area

$$A_{\mathrm{v}} = \frac{V^{\frac{2}{3}} V_{\mathrm{L}}^{\frac{1}{3}} (\mathrm{d}P_{\mathrm{ex}}/\mathrm{d}t)_{P_{\mathrm{red}},\,V_{\mathrm{L}}}}{C_{\mathrm{d}}(2RT/M)^{\frac{1}{2}} P_{\mathrm{red}}^{\frac{1}{2}} (P_{\mathrm{red}} - P_{\mathrm{a}})^{\frac{1}{2}}} \qquad [17.48.21]$$

where P_a is atmospheric pressure. From this equation the pressures are evidently absolute pressures.

A corresponding equation may be derived for the adiabatic case using Equation 17.12.55.

The method requires the specification of a suitable value of $(\mathrm{d}P_{ex}/\mathrm{d}t)_{P_{red},\,V_L}$ for use in Equation 17.48.21. In general, this term is a function of the maximum rate of pressure rise:

$$\left(\frac{\mathrm{d}P_{\mathrm{ex}}}{\mathrm{d}t}\right)_{P_{\mathrm{red}},\,V_{\mathrm{L}}} = K_{\mathrm{f}}\left(\frac{\mathrm{d}P_{\mathrm{ex}}}{\mathrm{d}t}\right)_{\mathrm{max},\,V_{\mathrm{L}}} \qquad [17.48.22]$$

where K_f is a constant. The values of K_f recommended for use in Equation 17.48.22 are given in Table 17.70.

The nomograph due to Heinrich for the estimation of vent areas is shown in Figure 17.125.

Table 17.70 *Dust explosion venting: the Heinrich K_f parameter*

Vent opening pressure (bar)	*Maximum rate of pressure rise in closed vessel,* $(dP_{ex}/dt)_{max,\ VL}$ (bar/s)	K_f
1.15	1000	0.5
	2000	1.0
1.6–1.8	1000	0.5
	1000–2000	0.67
	2000	1.0

As stated earlier, the Bartknecht nomograph method draws on this work.

17.48.14 Palmer method

The method given by K.N. Palmer (1974c) takes as its starting point experimental measurements on the maximum closed explosion pressure and rate of pressure rise for the dust mixture. He considers two cases: a low pressure case where the venting pressure is close to atmospheric and a high pressure case.

For the low pressure case the venting pressure is close to atmospheric:

$$P/P_o \approx 1 \qquad [17.48.23]$$

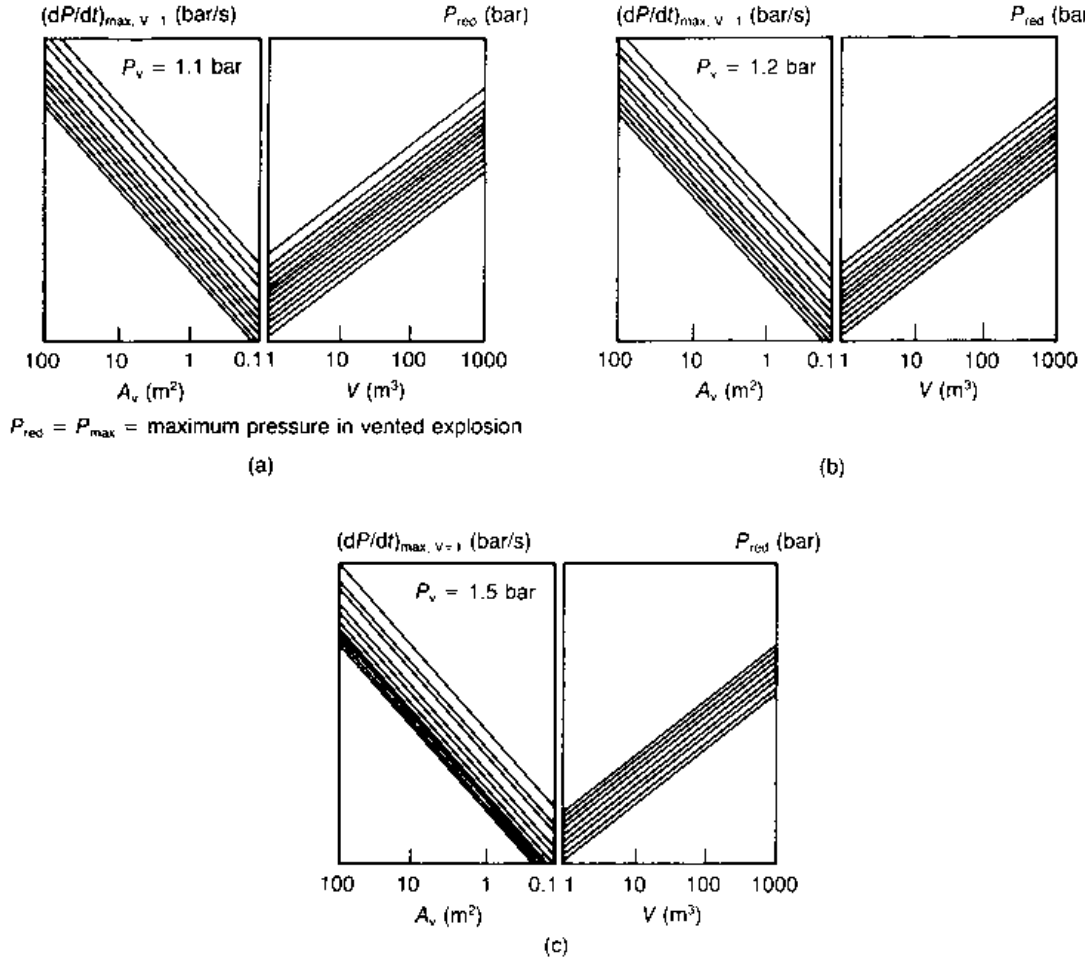


Figure 17.125 *Dust explosion venting: Heinrich nomographs for vent area (Lunn, 1984b; after Heinrich, 1974) (Courtesy of the Institution of Chemical Engineers)*

where P_o is atmospheric pressure. For this case Palmer uses Equation 17.12.63 for the mass velocity G_v of vent outflow. Then utilizing relation 17.48.23

$$G_v \approx C_d[2P_o\rho_o \ln(P/P_o)]^{\frac{1}{2}} \quad [17.48.24]$$

where C_d is the coefficient of discharge and ρ_o is the density of the gas at atmospheric pressure. From these equations the pressures are evidently absolute pressures.

In the closed vessel at the point where the rate of production of burned gas is at a maximum, the rate of pressure rise is $(dP/dt)_{max}$, the corresponding pressure is P_c and the rate of volume production is

$$\frac{V}{P_c}\left(\frac{dP}{dt}\right)_{max} \quad [17.48.25]$$

He takes account of the fact that with venting combustion conditions approximate to constant pressure rather than constant volume by introducing the ratio of specific heats γ. Then writing

$$\rho = \rho_o P/P_o \quad [17.48.26]$$

the maximum mass rate of production is

$$\frac{PV\rho_o}{P_o\gamma P_c}\left(\frac{dP}{dt}\right)_{max} \quad [17.48.27]$$

Then equating this rate of mass rate of production with the mass vent outflow given in Equation 17.48.24 and utilizing the relation

$$\rho_o = \rho_c = P_a/P_c \quad [17.48.28]$$

and the empirical relation

$$P_c = 0.6P_{max} \quad [17.48.29]$$

gives

$$P - P_o = \frac{2.3P_o\rho_c}{C_d^2\gamma^2P_{max}^3}\left(\frac{V}{A_v}\right)^2\left(\frac{dP}{dt}\right)_{max}^2 \quad [17.48.30]$$

where A_v is the vent area and the subscript c refers to the point at which the maximum rate of pressure rise occurs. Palmer defines the density ρ_c as the density of the unburned gas at P_o and as that of the combustion products at P_c. Equation 17.48.30 is the equation for the low pressure case.

For the high pressure case the mass velocity of venting is given by Equation 17.12.55. Then utilizing relation 17.48.23 and rearranging,

$$G_v = C_d\left[\frac{\rho_o\gamma}{P_o}\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(\gamma-1)}\right]^{\frac{1}{2}}P \quad [17.48.31]$$

$$= KP \quad [17.48.32]$$

with

$$K = C_d\left[\frac{\rho_o\gamma}{P_o}\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(\gamma-1)}\right]^{\frac{1}{2}} \quad [17.48.33]$$

Also for this case the author takes the mean mass velocity of venting as

$$G_{v,\,av} = \frac{K}{2}(P - P_o) \quad [17.48.34]$$

The duration of the explosion in the closed vessel, from ignition to maximum pressure, is

$$\frac{P_{max} - P_o}{(dP/dt)_{av}} \quad [17.48.35]$$

where P_{max} is the maximum unvented explosion pressure and the subscript av denotes average. Then from Equations 17.48.34 and 17.48.35 the total mass vented is

$$\frac{KA_v}{2}\frac{(P - P_o(P_{max} - P_o)}{(dP/dt)_{av}} \quad [17.48.36]$$

The total mass originally present was $V\rho_c$. Hence the fraction of the mass remaining is

$$1 - \frac{KA_v}{2}\frac{(P - P_o)(P_{max} - P_o)}{V\rho_c(dP/dt)_{av}} \quad [17.48.37]$$

Utilizing the empirical relation

$$\left(\frac{dP}{dt}\right)_{av} = 0.4\left(\frac{dP}{dt}\right)_{max} \quad [17.48.38]$$

Equation 17.48.37 gives for the fraction of mass remaining

$$1 - KA_v\frac{(P - P_o)(P_{max} - P_o)}{0.8V\rho_c(dP/dt)_{max}} \quad [17.48.39a]$$

$$= \frac{P}{P_{max}} \quad [17.48.39b]$$

Utilizing the relations

$$P_{max},\ P \gg P_o \quad [17.48.40]$$

Equation 17.48.39 becomes

$$\frac{1}{P - P_o} = \frac{1}{P_{max} - P_o} + \frac{KA_vP_{max}}{0.8V\rho_c(dP/dt)_{max}} \quad [17.48.41]$$

Equation 17.48.41 is the equation for the high pressure case.

17.48.15 Rust method

Another method described in Section 17.12 is that of Rust (1979). This method was in fact derived originally for the venting of dust explosions in low strength plant. For a dust mixture initially at atmospheric pressure

$$P = \frac{K_Dt^3}{V} \quad [17.48.42]$$

with

$$K_D = \frac{4}{3}\pi u^3P_{max} \quad [17.48.43]$$

where K_D is an explosion parameter, P is the absolute pressure, t is the time, u is the velocity of the flame front, V is the volume of the vessel and the subscript max denotes maximum.

Then, as before, the vent area is

$$A_v = \frac{kF(P_{max}V)^{\frac{2}{3}}K_D^{\frac{1}{3}}}{P_{red}^{\frac{1}{2}}} \quad [17.48.44]$$

where P_{red} is the reduced pressure (gauge) and k is a constant. The value of k is given in Section 17.12.

The parameter K_D may be determined from the pressure rise in tests. Thus, differentiating Equation 17.48.42 gives

$$\frac{dP}{dt} = \frac{3K_D t^2}{V} \qquad [17.48.45]$$

17.48.16 Nagy and Verakis method

The model given by Nagy and Verakis (1983), described in Section 17.12, is applicable to dust explosions. Using the notation given in Section 17.12, for explosion venting of a cylinder with an open vent, with ignition at the closed end, with subsonic flow and with venting of burned gas

$$\frac{P_{red}}{(P_{red} - P_o)^{\frac{1}{2}}} = \frac{RT_u k_{v1} P_o L(A_v/V)}{T_b^{\frac{1}{2}} \alpha S_u (P_m - P_o)} \qquad [17.48.46]$$

The left hand side term in Equation 17.48.46 is termed the pressure coefficient. For dust explosions it may be measured directly.

For venting with an initially closed vent, Equation 17.48.46 becomes

$$\frac{P_{red} + P_v}{(P_{red} - P_o)^{\frac{1}{2}}} = \frac{RT_u k_{v1} P_o L(A_v/V)}{T_b^{\frac{1}{2}} \alpha S_u (P_m - P_o)} \qquad [17.48.47]$$

where ΔP_v is the vent overpressure at which the vent opens ($lb_f/in.^2$).

17.48.17 Elongated vessels

There is relatively little information available on the dust explosion venting of elongated vessels. Most treatments are either for compact vessels or for pipes.

17.48.18 Critique of available methods

The methods available for the estimation of the vent area for a given reduced explosion pressure have been reviewed by Lunn (1984b). Of the empirical methods, his preferred methods are the K_{st} nomograph method and, where suitable data are available, the Schwab and Othmer method.

The theoretical methods all rely more or less heavily on experimental data. Lunn finds that the Heinrich method gives upper limits of the reduced pressure for St 1 and 2 dusts, but should not be used for St 3 dusts. The Palmer method gives good predictions for St 1 and 2 dusts, but tends to underestimate the reduced pressure for St 3 dusts in larger vessels. The Rust method is better for St 1 dusts than for St 2 and 3 dusts, and can be highly inaccurate in some cases. The Pittsburgh method requires information on the burning velocity and turbulence factor which are generally not available and is of limited application.

For silos Lunn states that the only available method is that given in VDI 3673, which tends to overestimate the vent area. He suggests that the Rust method may also be used for quiescent conditions.

In his later treatment, Lunn (1992) concentrates on the Bartknecht nomograph, the vent ratio and venting coefficient, or K factor, methods.

17.48.19 Venting of low strength plant

The maximum safe pressure for much plant handling dusts is 15 kPa ($2\,lb_f/in.^2$), and this maximum pressure is used in some of the design methods. Dust-handling plant is often constructed, however, in thin metal sheet which is unable to withstand pressures of more than 7 kPa ($1\,lb_f/in.^2$), even if the large flat sections of plant are provided with additional stiffening.

There is some difference of practice between the UK and the USA on the one hand and continental Europe on the other. Plant in the latter tends to be designed to a somewhat higher pressure rating.

Several authors have addressed the problem of dust explosion venting for low strength plant. The method given by Rust (1979) is explicitly intended for this application. The worked example given by Rust is for a filter with a maximum allowable pressure of 23.9 kPa (3.47 psi).

The lowest reduced pressure for which the Bartknecht nomographs apply is 0.2 barg, but, as already described, Lunn, Brookes and Nicol (1988) have extended the nomograph method down to reduced pressures of 0.05 barg, or even less.

17.48.20 Venting phenomena

If the vent is an open one, venting will result in the emergence of a flame. With a dust the flame tends to be considerably larger than with a gas. This is illustrated by the series of photographs given by Bartknecht (1981a) for gas and dust explosion venting.

If the vent has a duct, there is the potential of unburned dust to undergo combustion, possibly resulting in overpressure in the duct.

17.48.21 Vent design and details

In general terms, the design of vents for dust explosion venting and the details of the vents are similar to those used for gas explosion venting. Details are given in NFPA 68: 1994.

17.48.22 Vent ducting effects and design

As described in Section 17.12, the vent duct can have a marked effect on the maximum pressure in a vented explosion.

Figure 17.126 given by Bartknecht (1981a) shows the effect of dust class, dust concentration and duct length on the reduced pressure in a $2\,m^3$ vessel with a vent area of $0.13\,m^3$.

The general recommendations given by Bartknecht for vent ducts apply to gases and dusts. The vent duct should be straight, as short as practicable and preferably cylindrical. It should have the same pressure rating as the vessel. Since detonations may develop in pipes of 10–30 m length, the vent duct should be limited to 10 m. Reaction forces should be allowed for.

A graph to determine the maximum allowable length of smooth, straight pipe or vessel which is closed at one end and vented at the other which is applicable to propane and to dusts is given in NFPA 69: 1994 and has been given as Figure 17.36. If the L/D ratio is greater than that shown, there is a risk of detonation. There are separate curves for dusts with $K_{St} \leq 200$ and $K_{St} > 200$ bar m/s.

There are available several correlations to assist in allowing for the effect of the vent duct. Figure 17.127 given by Bartknecht (1981a) gives the relationship between the reduced pressure with the duct versus that without the duct. There are two lines, the parameter

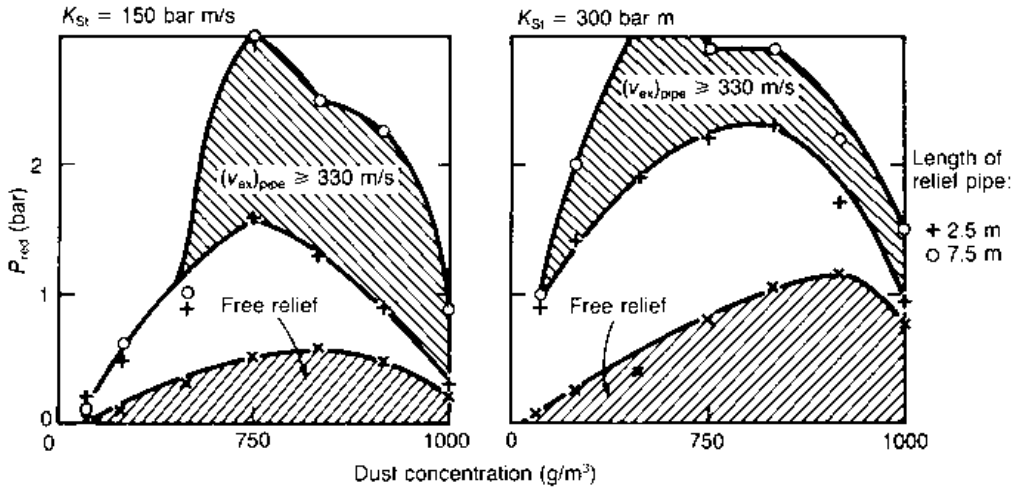


Figure 17.126 *Dust explosion venting: effect of dust explosibility and concentration and of length of duct on reduced pressure (Bartknecht, 1981a). Vessel volume 2 m^3, vent area 0.13 m^2 (Courtesy of Springer-Verlag)*

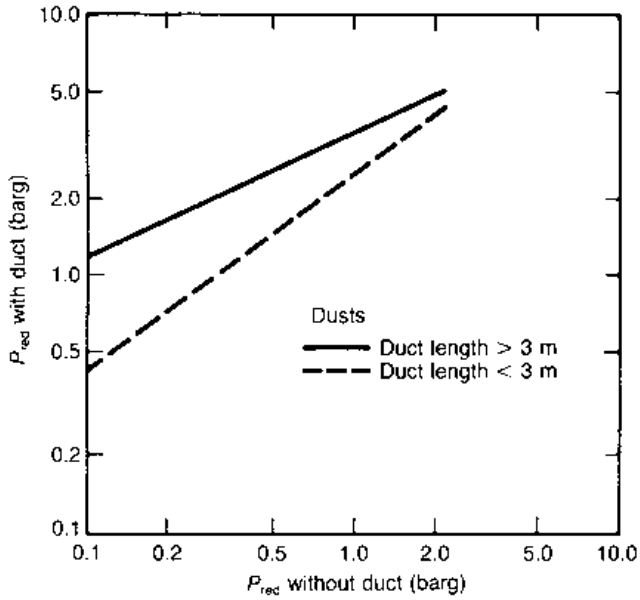


Figure 17.127 *Dust explosion venting: effect of length of vent duct on reduced pressure (NFPA 68: 1994). See text for details and note to Figure 17.25 (Reprinted with permission from NFPA 68 Deflagration Venting, Copyright © 1994, National Fire Protection Association, Quincy, MA 02269).*

being the duct length. Figure 17.128 gives a further correlation for the same relationship, but in this case the parameter is the gas velocity. Both correlations were given in NFPA 68: 1988, but only the first is retained in NFPA 68: 1994.

Figure 17.129, also given in NFPA 68: 1994, shows the maximum explosion pressure developed in deflagration of dust in a smooth, straight pipe open at one end with an initial flow velocity of less than 2 m/s.

17.48.23 Safe discharge

Explosion venting gives rise to three effects: a pressure wave and discharges of flame and of unburned material. It is essential that all three effects be handled safely.

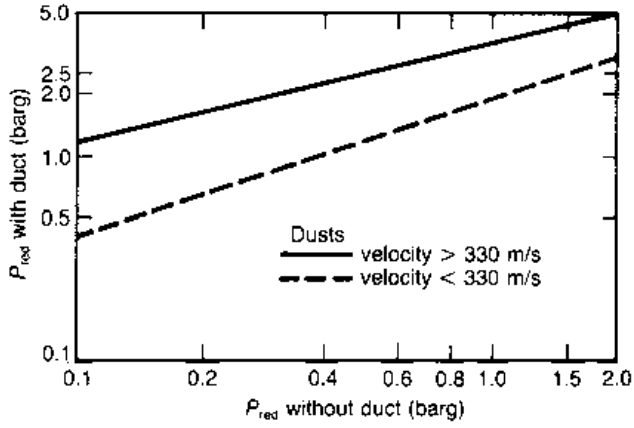


Figure 17.128 *Dust explosion venting: effect of velocity in vent duct on reduced pressure (NFPA 68: 1988). See text for details and note to Figure 17.25 (Reprinted with permission from NFPA 68 Deflagration Venting, Copyright © 1988, National Fire Protection Association, Quincy, MA 02269).*

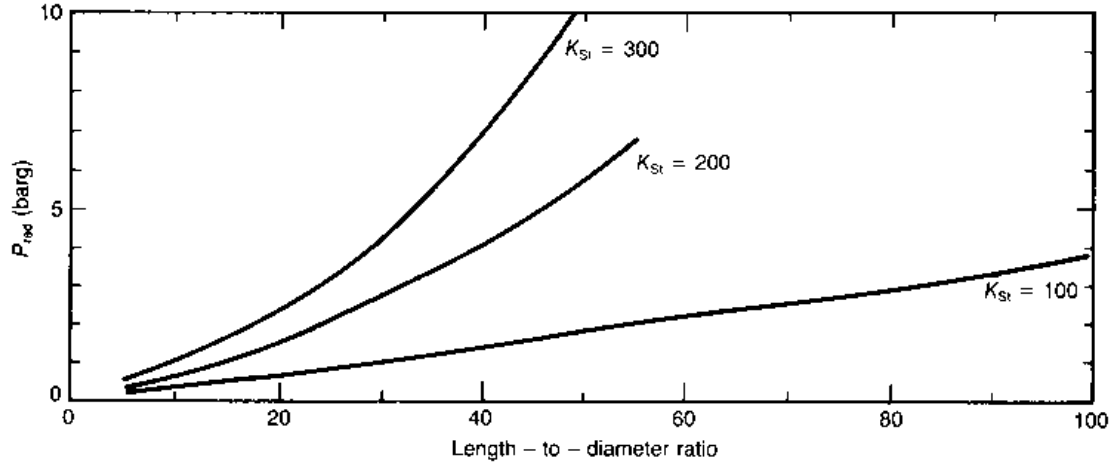


Figure 17.129 *Dust explosion venting: reduced explosion pressure in deflagration of dust/air mixtures in a smooth, straight pipe or duct closed at one end (NPFA 68: 1994). See text for details and note to Figure 17.25 (Reprinted with permission from NFPA 68 Deflagration Venting, Copyright © 1994, National Fire Protection Association, Quincy, MA 02269).*

The discharge of unburned dust can be particularly strong and can result in a large flame. With dusts the problem of the toxicity of the vented material can be particularly severe.

17.48.24 Dust explosion venting of ducts and pipes

The gas explosion venting of ducts and pipes was considered in Section 17.13. There is relatively little guidance available on dust explosion venting of ducts and pipes.

Early work by K.C. Brown (1951) on elevator casings showed a general similarity between gas explosions and dust explosions and the value of vents near the point of ignition.

In his discussion of explosion venting of pipes, Bartknecht (1981a) states explicitly that the course of gas and dust explosions in pipes is similar and that his recommendations for explosion venting apply to all combustible materials.

Lunn (1984b) recommends that in the absence of specific information for dusts the guidelines for gas explosion venting be used.

Dust-carrying pipelines will generally require multiple vents. NFPA 68: 1988 and 1994 gives guidance on the spacing of vents. This is shown in Figures 17.38 and 17.39, which apply to propane and dusts.

The treatment given in the IChemE *Dust Explosion Venting Guide* is based on these graphs.

17.48.25 Dust explosion venting of buildings

The strength of buildings is discussed in Section 17.8. A pressure of 7 kPa (1 psi) is often quoted as sufficient to destroy a typical brick building.

Methods for the explosion venting of buildings are discussed in Section 17.14. The two principal methods for the gas explosion venting of buildings are those of Rasbash and of Runes. The Runes method is that most often mentioned for the dust explosion venting of buildings and is that given for that purpose in NFPA 68: 1978. The use of the Runes equation for the explosion venting of buildings was described in Section 17.14 and the values of the Runes constant C for dusts were given in Section 17.48.10.

17.49 Dust-Handling Plant

Operations in which dusts are generated or handled include

(1) size reduction;
(2) conveying –
  (a) manual,
  (b) mechanical,
  (c) pneumatic;
(3) separation –
  (a) settling chambers,
  (b) cyclones,
  (c) filters,
  (d) scrubbers,
  (e) electrostatic precipitators;
(4) driers –
  (a) tray driers,
  (b) rotary driers,
  (c) fluidized bed driers,
  (d) pneumatic driers,
  (e) spray driers;
(5) screening and classifying;
(6) mixing and blending;
(7) storage;
(8) packing;
(9) fired heaters.

In many cases, there is a choice of different methods of carrying out a particular operation. The hazard of a dust explosion should be a factor in selecting a suitable method.

All plant handling flammable dusts should have a combination of sufficient strength and explosion protection to withstand a dust explosion safely.

Some other basic principles in the design and operation of dust-handling plant are (1) minimization of space filled by dust suspensions, (2) maintenance of design operating conditions, (3) minimization of mechanical failure and overheating, (4) precautions against static electricity and (5) precautions against passage of burning dust.

Some particular types of dust-handling plant, namely grinding mills, conveyors, dust separators, driers and storages, are considered below.

Operations involving screening and classifying or mixing and blending tend to create dust suspensions. Plant for such operations should be enclosed and preferably run under a slight vacuum. Precautions should be taken against static electricity and explosion protection should be provided.

Where dusts such as pulverized coal are used as fuels for fired heaters or furnaces, an explosive dust suspension is burned under controlled conditions. As with other fuels the principal hazard is loss of ignition followed by re-ignition and explosion.

Accounts of the safe design of dust-handling plant are given by K.N. Palmer (1973a), Bartknecht (1981a) and Field (1982).

17.49.1 Grinding mills

There is a large variety of size reduction equipment from jaw crushers to micronizers. In equipment which produces powders or dusts by size reduction, there is inevitably a real possibility of a dust explosion. The dust concentrations in a mill may be in the explosive range and the grinding elements in the mill, or possibly foreign bodies, may act as sources of ignition.

There are various steps which can be taken to minimize the dust explosion hazard in a mill. The free volume should be kept low so as to avoid a large volume of dust of explosible concentration. Large free volumes can occur if the mill is oversized or the feed to the mill is too low.

Overloading of or blockage in the mill can cause it to run hot and give ignition. The motor should be protected with an overload trip.

In general, mills are relatively robust. Even the larger mills with a volume of some tens of cubic metres can be designed to withstand pressures up to 350 kN/m^2 (50 lb$_f$/in.^{2}). However, explosion relief should be provided if necessary.

Bartknecht (1981a) gives three designs for complete grinding mill systems with respectively inerting, explosion suppression and explosion venting.

17.49.2 Conveyors

Dust may be conveyed by manual methods or by mechanical or pneumatic conveyors.

Applications of manual dust handling are restricted largely to operations such as bagging up of dust products or removal of unwanted dusts in limited quantities. There should be good local ventilation at places where dust may be generated such as bagging points and there should be a high standard of housekeeping on the plant.

Methods of mechanical conveying include screw and drag-link conveyors, belt conveyors and bucket elevators. A screw conveyor has minimal free volume and is an effective conveyor for dusts. So also is a drag-link conveyor, although the return leg contains free space which usually requires explosion protection. A belt conveyor is suitable for dusts only if enclosed. The free volume within the enclosure is likely to be larger than for a drag-link conveyor and the hazard correspondingly greater. If a belt conveyor is used, the enclosure should have explosion protection.

All mechanical conveying methods involve the risk of overheating due to mechanical failure, and appropriate steps should be taken in design and operation to minimize this hazard. In addition, belt conveyors are particularly liable to generate static electricity, and suitable safeguards should be provided.

17.49.3 Bucket elevators

The use of a bucket elevator to convey dust involves severe hazards unless there are suitable safeguards. There have been a number of explosions in bucket elevators and, as already mentioned, one of the few pieces of work on dust explosions in ducting is the work of K.C. Brown (1951) on elevator casings. Precautions for bucket elevators are discussed by K.N. Palmer (1973a) and Field (1982).

A bucket elevator tends to have a dust suspension virtually continuously, particularly at the boot and the head. The ignition source for an explosion is commonly a slipping belt or impact of the buckets on the casing.

Features of design to minimize the hazard include the provision of separate delivery and return legs, making the casing dust tight and able to contain fire, provision of isolation chokes at both ends, and location of the elevator outside the building.

Explosion suppression may often be a suitable option, particularly if the elevator is inside a building. For explosion venting, Field recommends a vent ratio of $\frac{1}{6}\,m^2/m^3$ with vents at the boot and head and, if the elevator is longer than 6 m, vents at intervals along it.

17.49.4 Pneumatic conveying

There are two basic systems for pneumatic conveying described by K.N. Palmer (1973a). These are (1) low volume/high pressure air and (2) high volume/low pressure air. The high pressure system uses relatively strong piping. It may be possible, therefore, to design it to withstand a dust explosion. There may be a risk, however, of erosion and consequent thinning of the pipe wall. The low pressure system utilizes weaker pipework and usually requires additional explosion protection such as vents.

Field (1982) states that in most pneumatic conveying systems the dust concentration is normally operated well above the upper explosive limit, though this may not apply at start-up and shutdown, and that the pipework is of a sufficient rating to withstand the full explosion pressure. The application of explosion protection is therefore mainly to the plant connected to the conveying system.

Precautions against ignition by static electricity or burning dust are particularly important in pneumatic conveying systems.

Further aspects of dust explosion hazards in pneumatic conveying systems are described by Palmer and Field.

17.49.5 Dust separators

In selecting a method of separation of a dust from a gas an important factor as far as dust explosions are concerned is the free volume. A settling chamber tends to involve a rather large free volume and usually is not a very desirable method.

Two of the main types of dust separator are dust filters and cyclones, which are considered below.

For both types of separator, precautions against ignition by static electricity or burning dust are especially important.

An alternative type of separator, in which the dust explosion hazard is much reduced, is the wet scrubber. Thus in the UK the use of wet scrubbers has been a statutory requirement in the grinding of magnesium. Wet scrubbers are used mainly to remove unwanted materials.

High efficiency cleaning of gases is often effected by an electrostatic precipitator. Although the inlet concentration of dust is normally below the explosive limit, mechanical rapping of the electrodes can create an explosive dust concentration. Electrostatic precipitators are not generally very suitable for removal of flammable dusts.

17.49.6 Dust filters

A widely used separation device is the bag filter. Such filters may be fitted after a cyclone or on their own. An explosive concentration of dust is liable to arise in bag filters which are cleaned by mechanical shaking and occurs during the cleaning operation. Again the ignition source may be dust ignited elsewhere.

Precautions for dust filters are discussed by K.N. Palmer (1973a), Bartknecht (1981a) and Field (1982).

Explosion suppression is an option which may have merit for a dust filter. For explosion venting, Field indicates that the volume on which the venting is based should be the free volume, or total volume less the volume of the filter bag assembly. Where the filter is lightly constructed, he states that the vent ratio method is suitable for smaller volumes ($< 30\,m^3$), but that the vent coefficient method is preferable for larger volumes, whilst where the filter is able to withstand a reduced explosion pressure of 0.2 barg, the regular K_{st} nomograph method is suitable. He also says that there is evidence that the nomograph method may overestimate the vent area, absorption of heat by the filter bags being a possible factor in this. The location of the vent is important in the case of dust filters. For the filter configuration which he considers, vents on the top tend to be less effective due probably to the obstacle-induced turbulence as flame propagates through the filter assembly. His recommendation is for vents located near the bottom of the rear side.

Bartknecht gives an account with detailed design of several filters.

17.49.7 Cyclones

Another common means of separation is the cyclone. Explosions in plant handling dusts occur not infrequently at a cyclone. Often the source of ignition is not at the cyclone itself but dust ignited elsewhere in the plant.

Precautions for dust cyclones are discussed by K.N. Palmer (1973a), Bartknecht (1981a) and Field (1982).

In a cyclone there is a concentration gradient of dust with a very low concentration at the wall. At some intermediate point the dust concentration is in the explosive range. This unique pattern of dust concentration could mean that the usual correlations for dust explosion venting may be less applicable. On the other hand, the explosion pressure in a cyclone may well arise due to ignition elsewhere in the plant and in this case the normal dust pattern in the cyclone may be disturbed.

For cyclones with the product offtake connected to other plant as in a spray drier system, Bartknecht recommends an isolation choke on product offtake.

Explosion suppression is an option which can be considered for cyclones. For explosion venting, Field

refers to work by K.N. Palmer (1974b) and Tonkin and Berlemont (1972 FRS Fire Res. Note 942) showing that the vent ratio method tends to overestimate the vent area. Cyclones are often of too light a construction for the regular K_{st} nomograph method to be applicable. The vent is most effective if located on the top of the cyclone.

17.49.8 Driers

There are a large number of different types of drier, but there are certain common hazards. These types include (a) tray driers, (b) rotary driers, (c) fluidized bed driers, (d) pneumatic driers and (e) spray driers.

Precautions for driers are discussed by K.N. Palmer (1973a), Bartknecht (1981a) and Field (1982). The IChemE *Drier Guide* also gives detailed guidance.

In many driers, the liquid driven off is itself a flammable vapour and constitutes an explosion hazard. The main method of prevention is to use ventilation to keep the vapour concentration well below its lower flammability limit.

Direct firing of driers creates a strong ignition source and for this reason indirect heating is often used instead.

Other hazards in driers arise if the plant is not operated according to design conditions. Thus if the feed rate is low, the material may become overheated and may ignite. Overheating may also occur if material from a previous batch is exposed to hot air on start-up. Similar hazardous conditions can arise in shut-down or emergency situations. The control of drier operating conditions is therefore particularly important.

The hot product from a drier is another hazard. It may be necessary to cool it before storage if self-heating is to be avoided.

17.49.9 Fluidized bed driers

Fluidized bed driers may be batch or continuous. According to Bartknecht, incidents in such driers have mainly been with hybrid dust–gas mixtures.

The explosion suppression option is more difficult to apply to fluidized bed driers, because it is hampered by the high air velocities. Nevertheless, Bartknecht gives an account of its application.

For explosion venting, Field states that any of the three main methods, vent ratio, vent coefficient or regular K_{st} nomograph, may be used. He gives details of the optimum vent location.

Bartknecht gives an account with detailed design of several fluidized bed driers, including explosion suppression and explosion venting. Figure 17.130 shows one of his graphs for explosion venting, illustrating the effect of locating the explosion relief on the clean side of the dust filters.

17.49.10 Spray driers

In spray driers the dust concentration is usually calculated to be below the lower explosive limit, but air currents may create higher concentrations. Deposits of dried product may build up and may undergo thermal degradation or become contaminated with oil so that the ignition temperature is lowered. Ignition may occur if the air inlet temperature is too high or if part of the high speed atomizer breaks off and causes an incendive spark.

Precautions for spray driers are discussed by Bartknecht (1981a) and Field (1982).

These precautions include ensuring that the air inlet temperature is below the decomposition temperature of the product and that the product does not form layers which may undergo thermal degradation.

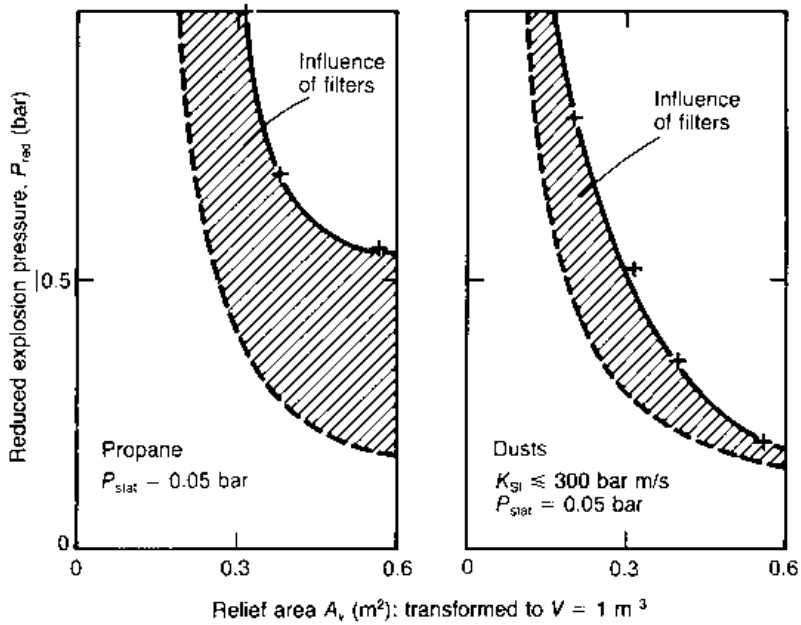


Figure 17.130 *Dust explosion venting: vent area requirement for a fluid bed drier (Bartknecht, 1981a) (Courtesy of Springer-Verlag)*

The atomizer should be regularly serviced. Other precautions against its acting as an ignition source are to monitor its vibration and the bearing temperature as well as the power consumption of its motor.

Inerting, explosion suppression and explosion venting are all options which may be used with spray driers.

Field states that if flammable solvents are present, the only suitable option is inerting. Explosion suppression is a suitable option for smaller volumes but he does not recommend it for larger ones. For explosion venting, he states that any of the three main methods, vent ratio, vent coefficient or regular K_{st} nomograph, may be used, although the vent ratio method overestimates the vent area for large volumes.

Bartknecht gives detailed designs for three complete spray drier systems, based respectively on inerting, explosion suppression and explosion venting.

In the particular design which he considers for the second of these options, explosion suppression is used in the drier and the cyclones and an extinguishing barrier in the pipe between the drier and the cyclones. All three are activated independently, and activation of any one causes shut-down. He states that design of an explosion suppression system for a volume $> 100\,m^3$ is a specialist matter.

In the design based on explosion venting, he considers first driers with $H/D < 5$. He states that for dusts a vent area may be used which is less than that given by the K_{st} nomograph method, since this tends to oversize the vent area for larger volumes. Moreover, the drier will never be full of an explosive dust suspension. For driers processing material with flammable solvents and thus containing hybrid dust–gas mixtures the nomograph for propane should be used, but the design is a specialist matter. For driers with $H/D > 5$ the vent area should be the whole roof.

For explosion venting, Bartknecht uses rapid action valves for isolation between the drier and the air heater and between the drier and the cyclones, and a rotary choke valve at the product offtake. Likewise he gives isolation arrangements for the explosion suppression case.

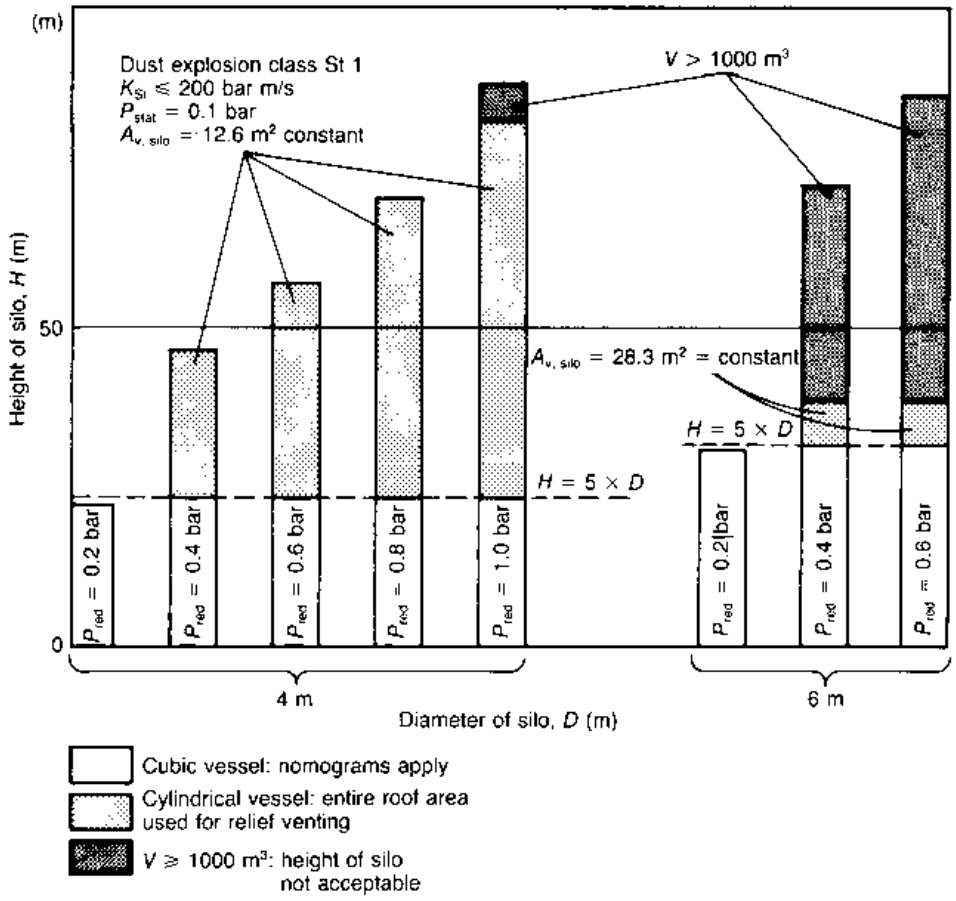


Figure 17.131 *Dust explosion venting: allowable height of a silo – 1 (Bartknecht, 1981a). The figure is based on the use of Bartknecht nomographs (Courtesy of Springer-Verlag)*

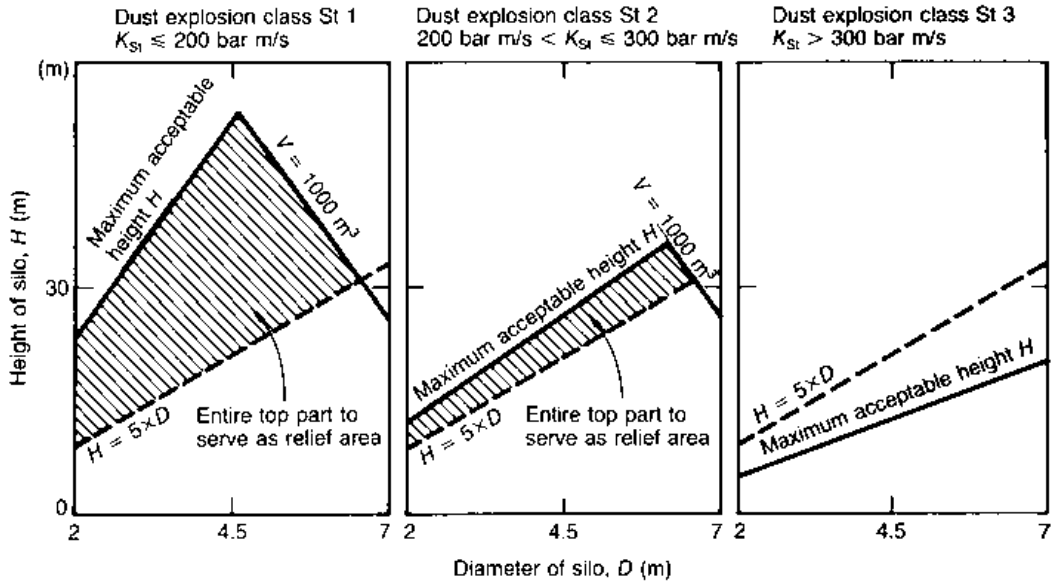


Figure 17.132 *Dust explosion venting: allowable height of a silo – 2 (Bartknecht, 1981a). The figure is based on the use of Bartknecht nomographs. $P_{stat} = 0.1$ bar; $P_{red} = 0.4$ bar (Courtesy of Springer-Verlag)*

He also emphasizes that in the event of an explosion there should be automatic shut-down and water sprinklers should be available to deal with the resultant dust fire.

17.49.11 Silos

As already described, a number of the principal dust explosions have occurred in silos. In a silo it is virtually inevitable that a dust suspension will exist in at least part of the space.

Precautions for silos are discussed by Bartknecht (1981a), Field (1982) and Eckhoff (1991).

A silo should be provided with feed arrangements which minimize the formation of dust suspensions. A silo may be filled by letting the dust fall from the roof or by introducing it down a vertical feeder duct so that it flows sideways onto the existing dust pile, the latter minimizing dust cloud formation.

The explosion suppression option is applicable to silos. Field states that it can be used effectively for volumes up to 60 m^3, but that beyond this careful consideration needs to be given to the dust explosibility and to the ability of the suppressant to fill the volume rapidly.

For explosion venting, Field states that the vent coefficient and regular K_{st} nomograph methods are applicable, but that the vent ratio method overestimates the vent area, and that none of the methods works well for H/D ratios greater than 3–5.

The explosion venting of silos has been considered in detail by Bartknecht. He treats it as an example of an elongated vessel and applies to it the principles which govern the venting of a pipe at one end. As with that case, the vent needs to be along the axis and to utilize the whole cross-sectional area of the end, which in this instance is the roof.

Bartknecht considers in particular the allowable height of the silo. This is essentially governed by two principles. One is that the cross-sectional area defines the maximum volume which can be vented and the other is that the maximum volume should be limited to 1000 m^3. Figures 17.131 and 17.132 illustrate the limits on the allowable height of a silo based on these principles.

17.49.12 Grain elevators

Other storages which have been the site of some of the main dust explosions are grain elevators. In consequence, there have been a number of studies of grain elevator explosions and of the precautions which should be taken.

In many incidents, poor standards of training, housekeeping and maintenance appear to have been major contributors.

The ignition sources identified in grain elevator explosions were given in Section 17.45.

Two of the principal components of grain elevators are the silos and the bucket elevator, both of which have just been discussed. Another main component is the horizontal conveyor, which conveys grain from the receiving point to the boot of the bucket elevator and from the offtakes of the silos to the loading point.

17.50 Dust Fires

It is convenient to deal at this point with dust fires. An account of dust fires is given by K.N. Palmer (1973a).

Dust fires occur in dust deposits and are of two types – flaming and smouldering fires.

The type of fire which is produced by a particular dust is not predictable and can only be determined by experiment, but some general guidelines can be given. A flame can be sustained only if sufficient volatile matter is evolved from the dust. If the dust is able to smoulder, the volatiles may be produced by this smouldering, otherwise they must be generated by the flame itself.

Characteristics of the dust which particularly affect this combustion process are volatile content, melting point and particle size.

The flame may spread across the surface of the dust or may burn down from the surface into the dust layer. If the flame is able to release sufficient volatiles, it may travel quite rapidly across the surface. Otherwise, its propagation over the surface is determined by the smouldering rate. Smouldering combustion may continue into the dust layer with the flame burning on the surface.

If the particle size of the dust is sufficiently large, the flame may propagate through the dust layer. In this case combustion is likely to be rather rapid.

On the other hand, a large particle size tends to give a low smouldering rate. In the limit the particle size may be too great for smouldering to persist.

Another feature which favours rapid combustion is an air flow. Such an air flow may be caused by ventilation or by convection currents, including those arising from the combustion process itself.

If a smouldering fire starts below the surface of the dust and works it way up, it may burst into flame and spread more rapidly when it reaches the surface.

Smouldering rates are commonly determined by measuring the rate of travel of smouldering combustion along a 'dust' train of stated dimensions. Typical smouldering rates for dusts are about 5 cm/h for wood and about 20 cm/h for coal with a bed depth of 1 cm. An extreme value is given by magnesium dust with a smouldering rate of 14 m/h.

There is a minimum depth of dust layer for sustained smouldering. Minimum depths typically range from approximately 2 mm upwards.

A dust deposit can undergo smouldering for a long period. It is not unknown for large dust piles to smoulder for a matter of years. Both air access and heat loss are restricted so that combustion is very slow, but is sustained. Such smouldering may give no readily detectable effects. In particular, there may be no smoke or smell from the burning.

This delay between ignition and outbreak of flaming can create hazards. Fire may break out unexpectedly in a factory shut down overnight or at the weekend, or the cargo of a ship may be discovered to be on fire when it is being unloaded.

Hazards of dust fires include those of a dust explosion resulting from the formation and ignition of a dust suspension, of the ignition of other flammables and of the evolution of toxic combustion products.

Fires in general dust deposits around the factory should be minimized by good housekeeping. As already indicated, the dust layer does not need to be very thick to sustain smouldering.

Detection of dust fires is difficult. There are no special types of detector for dust fires. The effects given by smouldering are usually weak and difficult to detect with the sensors normally used in automatic fire protection systems. It may be appropriate, however, to monitor the temperature in the interior of large dust piles with thermocouples.

Extinction of the dust fire may be effected by letting the fire burn itself out, by applying extinguishing agents or by starving the fire of oxygen.

Whichever approach is used, however, it is essential to avoid disturbing the dust in such a way as to allow a suspension to form and ignite.

Water is the usual extinguishing agent and is suitable unless it reacts with the dust or there is electrical equipment involved. The water should not be applied, however, as a high pressure jet, which could raise a dust cloud, but as a low pressure spray which simply dampens the dust deposit. The penetration of this water into the dust layer can be assisted by the addition of about 2% of a wetting agent such as a detergent.

The use of fire fighting foam generally offers little advantage over water. Foam has the additional capability of cutting off air to the fire, but this is unlikely to have much effect in a slow smouldering combustion which requires very little air anyway. Since the foam is largely water, it should not be used in applications where water is unsuitable.

The other non-gaseous fire fighting agents are of limited application. Dry powder is appropriate if the dust is one which reacts with water, as do some metal dusts. Vaporizing liquids are appropriate if electrical equipment is involved, but should not be used on reactive metal dusts.

Inert gases may be used as extinguishing agents and can be effective if the dust is held in a relatively gas tight container such as a hopper or a ship's hold. It is necessary, however, not only to cut off the supply of oxygen, but also to effect sufficient cooling to prevent re-ignition when the air supply is restored. Thus the inerting may need to be maintained for a long period.

In some situations, however, the fire cannot be extinguished sufficiently rapidly by fire extinguishing agents alone. A smouldering fire in a ship's hold, for example, could immobilize the whole ship. In such cases it may be necessary to dig the material out. This involves a number of hazards and suitable precautions should be taken against them. The operations should be conducted in such a way as not to raise a dust cloud. The atmosphere should be monitored and any necessary breathing equipment worn. The danger of subsidence of the dust due to the creation of burnt-out hollows beneath the surface should be allowed for.

In other instances a more gradual extinction of the fire is acceptable. This might be the case, for example, with a fire smouldering inside a tip. The methods used in such situations are generally based on excluding air and include covering the heap with a layer of non-combustible such as earth or pumping a limestone slurry into fissures in the heap. A hazard in the first method is subsidence due to hollows, and in the second, movement in the tip due to the slurry. Alternatively, but generally as a last resort, the heap may be dug out.

17.51 Explosion Hazard

The types of explosion typical of the process industries are those described above. The hazard of a large industrial explosion may be assessed by consideration

of assumed scenarios using appropriate hazard and effects models or of the historical record of explosions and their effects.

17.51.1 Historical experience

A large proportion of the major accidents which have occurred in the process industries have involved explosions. In particular, explosions account for the preponderance of cases where there has been substantial loss of life.

A classification of process industries explosions has been given in Section 17.1. The main heads are (1) physical explosions, (2) condensed phase explosions, (3) vapour cloud explosions, (4) BLEVEs, (5) confined explosions with reaction, (6) vapour escape into, and explosions in buildings and (7) dust explosions. Some principal condensed phase explosions have been listed in Table 17.24, vapour cloud explosions in Table 17.30, BLEVEs in Table 17.37 and dust explosion in Table 17.63. A fuller listing of all types of explosion with references is given in Table A1.2. The statistical features have been given in Chapter 2 and Section 17.1.

The process industries have suffered major explosions in virtually all the categories of the classification in Section 17.1. Considering these in turn, and starting with physical explosions, these may occur as (a) a mechanical failure, (b) overpressure, (c) underpressure, (d) overtemperature or (e) undertemperature of the system. The essential distinction is that in the first case the failure occurs whilst the process conditions are within the design envelope, so that the failure is due to a mechanical defect, and in the other cases it occurs because the process conditions have been taken outside the design envelope.

A failure of a pressure system due to mechanical defects occurred in 1984 at a refinery at Romeoville, Illinois, where a 55 ft high × 8 ft diameter absorption column suffered massive failure such that most of the 20 t vessel rocketed about 3500 ft and struck and toppled a 138 kV power transmission tower (Case History A111).

Overpressure of a pressure system is exemplified by the explosion at Grangemouth in Britain in 1987 when gas 'breakthrough' caused the disintegration of a 30 ft high × 10 ft diameter low pressure separator (Case History A116). One 3 t missile from this explosion travelled 3300 ft.

Condensed phase explosions in the process industries include explosions of (a) high explosives, (b) ammonium nitrate, (c) organic peroxides and (d) sodium chlorate. An account of condensed phase explosions has been given in Section 17.26.

With regard to high explosives, the explosion of the munitions ship *Mont Blanc* at Halifax, Nova Scotia, in 1917 destroyed a large part of the town and killed 1963 people (Case History A3). An explosion of TNT at a munitions factory in Silvertown, London, in 1917, caused 69 deaths (Case History A4).

Many of the large explosions in the early years of the chemical industry involved ammonium nitrate (AN). The AN explosion at Oppau, Germany, in 1921 destroyed hundreds of houses and killed 561 people (Case History A5).

The explosions at Texas City in 1947 occurred in two ships, the *Grandcamp* and the *High Flyer*, both of which were carrying AN (Case History A16). They damaged thousands of buildings, hurled missiles several miles and killed 552 people.

Major explosions involving organic peroxides occurred at Tonawanda, New York, in 1953 and Los Angeles in 1974 (Case History A72).

Two warehouse fires in Britain, at Renfrew in 1977 and Salford in 1982, resulted in large sodium chlorate explosions (Case History A85).

In recent years, the most destructive explosions in the process industries have tended to be VCEs or BLEVEs.

Some of the principal vapour cloud explosions have been described in Section 17.28. They include those at the Ludwigshafen works in 1953 and 1958, the refinery at Lake Charles in 1967, the refinery at Pernis in 1968, a pipeline at Port Hudson in 1970, a rail tank car at East St Louis in 1972, the works at Flixborough in 1974, the rail tank car at Decatur in 1974, a petrochemical plant at Beek in 1975 and a petrochemical plant at Pasadena in 1989. Flixborough and Pasadena are described in Appendices 2 and 6, respectively, and the other incidents in Appendix 1, as referenced in Section 17.28.

Some of the principal BLEVEs have been described in Section 17.29. Major incidents in which the BLEVE occurred due to release from the vessel involved or a similar, adjacent vessel, include those at a storage in Montreal in 1957, the refinery at Feyzin in 1966, a rail tank car at Crescent City in 1970, a refinery in Rio de Janeiro in 1972 and a storage at Texas City in 1978. Those at Feyzin, Crescent City and Rio are described in Appendix 1, as referenced in Section 17.29.

In other instances, BLEVEs have occurred as a result of engulfment in a major vapour cloud fire. Incidents where this was the case include those at the storage in Port Newark in 1951 (Case History A19) and at Mexico City in 1984 (Appendix 4).

Turning to confined explosions with reaction, these include (a) explosions involving vapour combustion, (b) reactor explosions and (c) other explosions involving liquid phase reactions. In the first category is the detonation in a 127 ft high × 22.5 ft diameter reactor at Whiting 1955 (Case History A22). The vessel disintegrated, hurling one 60 te fragment onto a tank farm 1200 ft away and causing two deaths.

There have been a large number of reactor explosions, usually incurring a medium level of casualties and loss. One of the more serious occurred at Geismar in 1976, when a large polygylcol ether reactor exploded, throwing the reactor head 1400 ft (Case History A80).

Liquid phase reactions occurring in other equipment have also led to major incidents. One such occurred at Doe Run in 1962, when backflow of ammonia from a reactor into an ethylene oxide feed tank resulted in a severe explosion (Case History A31).

Incidents of vapour escapes into, and explosions in, buildings (VEEBs) are exemplified by those at St Paul in 1951 and Attleboro in 1964 (Case History A33). In the first an escape of LPG at a loading terminal caused a explosion which killed 14 people. In the second a massive leak of vinyl chloride from a reactor into the building resulted in an explosion which led to seven deaths.

The explosion on Piper Alpha, which occurred in a partially confined module, might also be regarded as falling in this category (Appendix 19).

Finally, there have also been a number of serious dust explosions inside (a) plant and (b) buildings. An explosion inside a grain silo at Westwego in 1977 resulted in 36 deaths (Case History A89).

Most, though not all, of the incidents just described are in the *M&M Large Loss List*. Details of casualties and loss are given in Table A1.2.

17.51.2 Mortality index for explosions

The relation between the size of an explosion and the number of people killed has been investigated by V.C. Marshall (1977b), who has developed a mortality index (deaths/t) for explosions.

Data on the relation between the size of the explosion and the number of fatalities, and on the mortality index, are plotted in Figure 17.133. The solid squares which do not have a specific reference are accidental explosions. The full line is the best fit for these accidental explosions.

Mortality data on the number of casualties by shell explosions are available from the First World War. According to one account, the belligerants used 2.23×10^6 t of high explosive in 1.39×10^9 shells and caused 10^7 casualties. The latter figure includes wounded as well as dead, and the deaths are estimated as 2.4×10^6. Thus on average a shell contained 1.6 kg of explosive. Allowing for 10% dud shells, the fatalities per shell are approximately 0.0019, which gives a mortality index of 1.2.

The Second World War data for conventional bombing give mortality indices between 0.96 for Germany and 3.40 for Japan. This is no doubt influenced by factors such as population density, construction of houses and degree of shelter.

The mortality indices for the nuclear bombs at Hiroshima and Nagasaki are 2.05 and 1.0, respectively. The bombs were assumed to have a nominal yield each of 20 000 t of TNT.

The mortality indices of the Halifax explosion in 1917 and the Oppau explosion in 1921 are 0.64 and 0.25, respectively.

For accidental explosions the data used are the data given by C.S. Robinson (1944) and some unpublished data by Healy (1965), and they have been grouped by Marshall in size intervals.

As Figure 17.133 shows, the mortality index decreases as the size of the explosion increases. The line has a slope of about -0.5. This differs somewhat from the slope suggested by theoretical considerations. From the blast scaling laws the radius r at which a given blast intensity occurs is related to the mass of explosive W by the relation

$$r \propto W^{\frac{1}{3}} \qquad [17.51.1]$$

The number of fatalities f is proportional to the area:

$$f \propto r^2 \propto W^{\frac{2}{3}} \qquad [17.51.2]$$

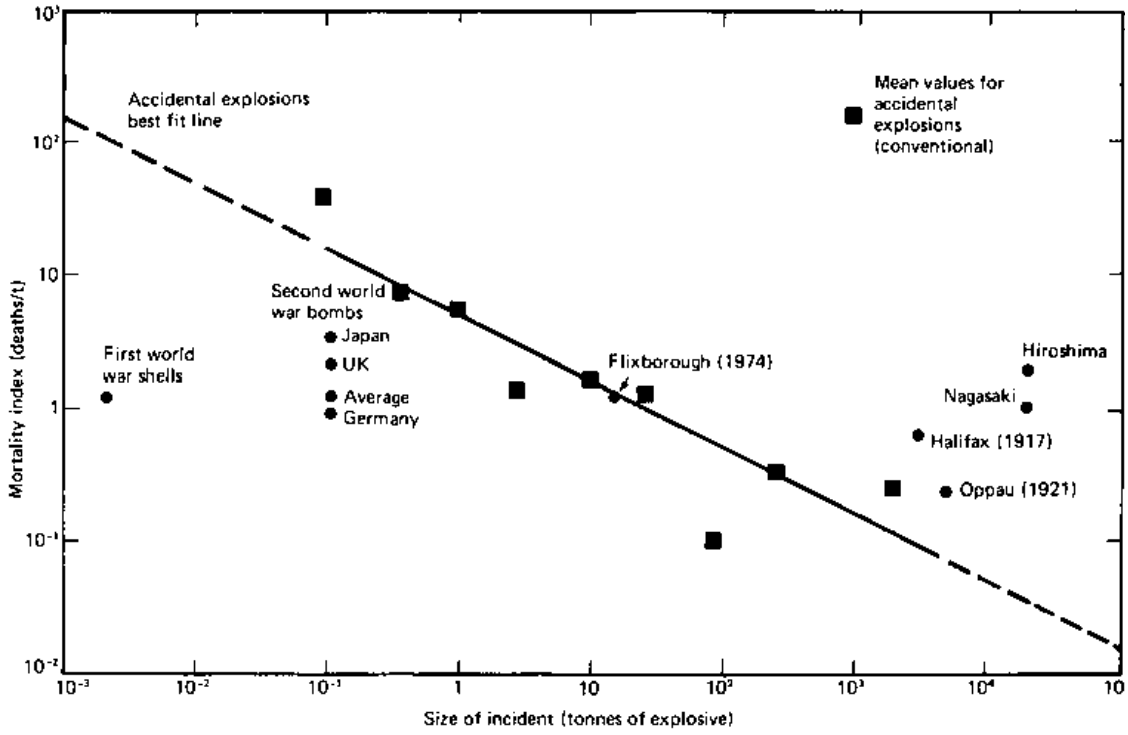


Figure 17.133 *Mortality index for explosions (after V.C. Marshall, 1977b) (Courtesy of the Institution of Chemical Engineers)*

The mortality index MI is the ratio of the number of fatalities to the mass of explosive:

$$\mathrm{MI} \propto \frac{f}{W} \propto W^{-\frac{1}{3}} \qquad [17.51.3]$$

Marshall suggests that a possible explanation is that small explosions which do not kill people tend not to be so well reported, which has the effect of exaggerating the mortality index for small explosions.

Vapour cloud explosions are also considered by Marshall, as shown in Table 17.71. Since for such explosions the TNT equivalent is generally unknown, the mortality index in this case is based on the mass of vapour involved.

Other aspects of historical experience with explosions are discussed in Sections 17.28–17.30 and 17.31–17.34.

17.51.3 Hazard assessment

Hazard assessment of explosion on process plants tends to be rather more varied than that of fire. As stated in

Table 17.71 *Some data on the relation between size of flammable release and number of fatalities (after V.C. Marshall, 1977b) (Courtesy of the Institution of Chemical Engineers)*

Date	*Location*	*Chemical*	*Material released*		*Nature of incident*	*Fatalities*	*Mortality index* (deaths/t)
			Liquid spilled (t)	*Vapour* involved (t)			
1943 Jan. 18	Los Angeles, CA	Butane		14	Fire	5	0.35
1944 Nov. 15	Cleveland, OH	LNG		180	Fire	213	1.18
1959 June 28	Meldrin, GA	LPG		18	Explosion and fire	23	1.27
1962 July 26	New Berlin, NY	LPG		17	Explosion and fire	10	0.58
1967[a] Aug. 6	Lake Charles, LA	Isobutane		13	Explosion	7	0.53
1968 Jan. 20	Pernis, Netherlands	Hydrocarbon vapour		50	Explosion	2	0.04
1970 Dec. 9	Port Hudson, MO	Propane		27	Explosion	0	0
1970 Oct. 23	Hull, UK	Propane	4	0.20	Fire	2	10.0
1971 July 11	Pensacola, FA	Cyclohexane		30	No ignition	0	0
1972 Jan. 22	East St. Louis, IL	Propylene		70	Explosion	0	0
1972 Mar. 19	Lynchburgh, VA	Propane	9	1.5	Fire	2	1.33
1972[a] Sep. 21	New Jersey	Propylene		18	Pressure rupture followed by fire	2	0.11
1973 Feb. 23	Austin, TX	Natural gas liquids	720	70	Fire	8	0.11
1974 June 1	Flixborough, UK	Cyclohexane	125?	40	Explosion	28	0.70
1974 June 29	Climax, TX	Vinyl chloride		75	Explosion	0	0
1975 Nov. 7	Beek, Netherlands	Propylene		5.5	Explosion and fire	14	2.54
Total of 16 incidents				630		316	
Mean of 16 incidents				39.4		19.7	0.49

[a] Date quoted in the original paper has been corrected (F.P.L.).

Section 17.1, explosions in the process industries include (1) physical explosions, (2) condensed phase explosions, (3) vapour cloud explosions, (4) BLEVEs, (5) confined explosions with reaction, (6) vapour escape into, and explosions in buildings and (7) dust explosions. The extent to which these different types of explosion are represented in the hazard assessment literature varies.

In principle, a hazard assessment involves formulation of a scenario and a full assessment of the frequency and consequences of the event. An assessment which is confined either to the estimation of the frequency of the event or to the modelling of the consequences is a partial one. Hazard assessments may be generic or may relate to a specific situation.

The scenario which has received most attention is the release and ignition of a vapour cloud, which may result either in a vapour cloud fire or a vapour cloud explosion. Thus the hazard assessment of vapour cloud explosions involves the development of a set of scenarios for explosion, by release and ignition, and of the associated event trees; the estimation of the frequency/probability of the initial events and of the events in the branches of the event trees from a mixture of historical data and synthesis of values, often using fault trees; and the modelling of the outcome events in the event tree, including both physical events and damage/injury.

Up to the point of damage and injury, the assessment of a vapour cloud explosion involves essentially the same set of models as those used for the modelling of vapour cloud fires, as described in Chapter 16. If the event gives an overpressure, it is a vapour cloud explosion, otherwise it is a vapour cloud fire.

A hazard assessment of the kind just described constitutes a full hazard assessment. The types of explosion which are most fully represented are high explosives and ammonium nitrate explosions, vapour cloud explosions and BLEVEs.

Overviews of generic process plant explosion scenarios have been given for LPG by Rasbash (1979/80) and Crocker and Napier (1988a) and for LNG by Napier and Roopchand (1986).

Some principal types of model used for hazard assessment of explosions on process plants are those for (1) condensed phase explosions, (2) explosions of vessels, (3) vapour cloud explosions, (4) BLEVEs and (5) dust explosions.

An early, essentially generic, hazard assessment of explosion is that given in the vulnerability model by Eisenberg, Lynch and Breeding (1975), who studied the area affected by a flammable vapour cloud and the lethality of a vapour cloud explosion in such a cloud. The events of principal interest which they consider are marine spillage of 20 750, 83 and 0.8 te of LNG on water with drifting of the vapour cloud towards populated areas. Their treatment of these scenarios is described in Chapter 16. For explosion injury they utilize their own probit equations described in Section 17.38. The populations at risk are defined in terms of the cell model already described. Some results obtained have been given in Chapter 16.

The First *Canvey Report* (HSE, 1978b) included assessments of the hazard at the specific installations at Canvey from an explosion of ammonium nitrate; a vapour cloud explosion from the British Gas LNG storage; and vapour cloud explosions from several LPG storages. These assessments were refined in the second report. An account of this work is given in Appendix 7.

The *Rijnmond Report* (Rijnmond Public Authority, 1982) gives specific hazard assessments for storages of acrylonitrile, propylene and LNG. It considers vapour cloud explosions and BLEVEs. An account of this work is given in Appendix 8.

The *Transport Hazard Report* of the Advisory Committee on Dangerous Substances (ACDS) (1991) gives hazard assessments for the transport of hazardous substances in ports, by road and by rail which are applicable to transport nationwide, although based in some cases on generalization from a sample of specific situations. The hazards covered include explosion of high explosives and of ammonium nitrate and vapour cloud explosions and BLEVEs from LPG and flammable liquids.

For physical explosions, hazard assessments have been mainly treatments of the frequency of explosion without modelling of the consequences. Studies of this type on specific plant have been described for overpressure of a storage tank by gas breakthrough by Kletz and Lawley (1982), overheating of a distillation column by Lawley and Kletz (1975) and undertemperature of a pipeline by Lawley (1980).

For condensed phase explosions, the hazard assessments of explosions of high explosives are represented by those in the ACDS study and of ammonium nitrate explosions by those in the *Canvey Reports* and the ACDS study. These are for specific situations, although in the ACDS study the results are then generalized.

For vapour cloud explosions and BLEVEs, there are a number of hazard assessments which cover these events. They include a generic study of storage installations by Considine, Grint and Holden (1982) and studies of specific installations by Panthony and Smith (1982) and Ramsay, Sylvester-Evans and English (1982).

There are also generic assessments of the frequency of BLEVEs by Drysdale and David (1979/80), Blything and Reeves (1988 SRD R488) and Selway (1988 SRD R492).

For confined explosions with reaction, hazard assessment of explosions involving vapour combustion include the estimations of explosion frequency for an ethylene oxide reactor system by R.M. Stewart (1971) and for a hydrocarbon sweetening plant by Kletz (1972a) and of explosion involving liquid phase reactors by Roy, Rose and Parvin (1984).

Vapour escapes into, and explosions in, buildings and dust explosions are not well represented in the hazard assessment literature.

17.52 Hazard Range of Explosions

The estimation of the hazard range of an explosion depends on the type of explosion considered.

The two main types of explosion of interest here are condensed phase explosions such as those of TNT, together with explosions which can be characterized in terms of TNT equivalent, and vapour cloud explosions.

17.52.1 Condensed phase explosions

The blast wave from a condensed phase explosion is characterized by the peak side-on overpressure and the impulse.

The variation of peak overpressure of a condensed phase explosion with distance is given by the scaling law and values of the overpressure may be obtained from graphs such as those given in Section 17.26. Thus

$$p^{o} = f(z) \qquad [17.52.1]$$

with

$$z = \frac{r}{W^{\frac{1}{3}}} \qquad [17.52.2]$$

where p^{o} is the peak overpressure, r is the distance, W is the mass of explosive and z is the scaled distance. Over a limited range the curve of p^{o} versus z may be approximated by a straight line so that

$$\frac{(\rho^{o})_{r}}{p^{o}} = \left(\frac{r_{r}}{r}\right)^{n} \qquad [17.52.3]$$

where n is an index and subscript r is reference value. From the Baker curve for the overpressure range 1.0—0.1 bar the index n is approximately 1.7. A similar approach may be used for the determination of the impulse.

The effects of the explosion may then be determined from the overpressure and impulse utilizing the methods given in Sections 17.31–35.

For housing damage, the variation of the degree of damage, or damage category, with distance may be obtained from the revision by Gilbert, Lees and Scilly of the Jarrett equation; this revision is given by Equation 17.33.2b with revised values of the constant k.

The graph given by C.S. Robinson (1944) and reproduced as Figure 17.92 summaries in convenient form the range of many of the principal damage effects.

17.52.2 Vapour cloud explosions

For a vapour cloud explosion, it is necessary to take into account the movement of the cloud, which is likely then to be the dominant factor.

The variation of cloud size with distance may be estimated from gas dispersion relations given in Chapter 15. An account is given there of the method of Considine and Grint (1985) which allows an estimate to be made of the size of the cloud for an LPG release.

Considine and Grint have also given for LPG methods for estimating the hazard range for fires and explosions. For a vapour cloud explosion they use the ACMH method based on the TNT equivalent. They give for the overpressure the relations

$$p^{o} = 138\left(\frac{I^{\frac{1}{3}}}{r_{c}}\right)^{1.558} \qquad r < r_{c};\ 0.05 < p^{o} < 1 \qquad [17.52.4a]$$

$$p^{o} = 138\left(\frac{I^{\frac{1}{3}}}{r}\right)^{1.558} \qquad r > r_{c};\ 0.05 < p^{o} < 1 \qquad [17.52.4b]$$

where I is the mass of vapour in the cloud (te), p^{o} is the peak overpressure (bar) and r_{c} is the radius of the cloud (m).

These authors quote from the First *Canvey Report* the estimates of 50 and 1% fatalities at overpressures of 0.36 and 0.18 bar, respectively. Within the cloud, 100% fatalities are assumed.

For a quasi-instantaneous release, the cloud range R and the cloud radius r_{c} vary with time. The mass I of vapour in the cloud is may be taken as the total mass released. The cloud is flammable, however, only whilst its concentration is within the flammable range.

For a quasi-continuous release, the approach taken is to treat the plume as if it were fully established. In this case the cloud is non-circular and the following relation is given for the equivalent value of cloud radius r_{c}:

$$r_{c} = \left(\frac{1.2k^{*}R_{LFL}^{\frac{5}{3}}}{\pi}\right)^{\frac{1}{2}} \qquad [17.52.5]$$

where R_{LFL} is the distance to the LFL (m) and k^{*} is a constant defining crosswind range. This constant is described in Chapter 15.

The TNT equivalent method for a vapour cloud explosion is obsolescent. More modern methods, particularly the TNO methods, are available, as described in Section 17.28, and may be preferred. However, the method of determining the cloud size may still be found useful.

In reality, for a vapour cloud explosion the peak overpressure is inversely proportional to the distance, and this is reflected in the more modern models. An illustration is the decay of the peak overpressure with distance shown in Figure 17.79(a).

17.53 Notation

Ma	Mach number
Re	Reynolds number
g	acceleration due to gravity
t	time
T	absolute temperature
γ	ratio of gas specific heats

Superscripts:

.	time derivative
..	second time derivative

Subscript:

max	maximum

Note:
(a) Some of these variables have different local definitions, for example: t (thickness of glass), T (time constant, natural period)
(b) The symbol R generally denotes the universal gas constant but is also used for distance, range. It is therefore not defined globally for the chapter

Section 17.2

Sections 17.2.3–17.2.9

a	velocity of sound
$\bar{c}_{v}$	mean specific heat at constant volume
D	velocity of shock wave
e	specific internal energy
Δe	specific internal energy change
h	specific enthalpy
i	impulse
p	absolute pressure
p_{pl}	plateau pressure
p_{v}	pressure of constant volume combustion
q	energy addition per unit mass

u	velocity
v	specific volume
V_1	velocity of gas entering shock wave
w	particle velocity
α	angle defined in Figure 17.1(d)
ξ	fractional completion of reaction
ρ	density

Subscripts:

CJ	Chapman–Jouguet condition
s	shock wave
1	entering shock wave
2	leaving shock wave

Section 17.2.10

a_o	velocity of sound in burned gas
d	diameter of tube
k_n	Bessel function derivative
p	pitch of spin
γ_o	ratio of specific heats of detonation products
λ	wavelength of spin

Sections 17.2.11 and 17.2.12

a_o	velocity of sound in mixture
d_c	critical diameter for transmission of detonation
E_c	critical energy for initiation of spherical detonation
L_c	length of detonation cell
L_i	length of induction zone
n	constant
S	width of detonation cell
Δ	induction length
τ_i	induction time
ϕ	fuel–air ratio

Subscripts:

l	lower limit
st	stoichiometric
u	upper limit

Section 17.2.13

c	velocity of sound
d_c	critical diameter for transmission of detonation
D_H	detonation hazard parameter
E_c	critical energy
E_c^*	minimum critical energy
p	absolute pressure
u	particle velocity
λ	stoichiometric ratio

Subscript:

D	detonation state

Section 17.2.15–17.2.17

c	velocity of sound in uncompressed gas
d	diameter of tube
d_c	critical diameter for transmission of detonation
d_{min}	minimum diameter of vapour cloud to support detonation
g_f	acceleration of flame
L_c	length of detonation cell
S_u	maximum fundamental burning velocity
X_d	run-up distance
X_f	distance from origin of flame to its position at time when shock first forms
X_s	distance from origin to position at which shock is produced
β	ratio of velocity of flow just ahead of flame to that of flame
γ	ratio of specific heats of reactant
ϵ	expansion ratio
θ_{cr}	critical angle for transition to regular reflection
θ_w	angle between shock wave travelling horizontally and a surface

Equations 17.2.56–17.2.57:

A_t	area of truncation
d	diameter of nozzle
D_{CJ}	C–J velocity
E_c	critical energy
L_c	length of detonation cell
p	pressure of planar detonation
S	width of detonation cell
t_c	time at which heads of expansio fan cross axis of symmetry
u_{CJ}	gas velocity behind C–J front
W	work done

Subscripts:

c	critical
CJ	C–J
o	actual

Section 17.3

Section 17.3.2

p^o	peak overpressure
r	distance
r_c	radius of crater
r_{50}	distance at which there is 50% chance of sympathetic detonation, mean detonation distance
R	radius of damage circle
W	mass of explosive
z	scaled distance

Section 17.3.3

k	constant
R	distance (ft)
W	mass of explosive (lb)

Section 17.3.4

Equation 17.3.8:

k	constant
n	index
R	distance
W	mass of explosive

Equations 17.3.9–17.3.11:

R	distance (ft)
W	mass of explosive (lb)

Section 17.3.5

B	blast effect
B^*	blast effect required for certainty of detonation
j	site counter
k	constant
n_1, n_2	indices
p	probability of further detonation
p'	parameter defined by Equation 17.3.15
$P(j)$	probability that j sites are involved in detonation
r	distance
T	threshold of p' below which no propagation occurs
W	mass of explosive

Section 17.4

A	Helmholtz free energy
E	internal energy
F	Gibbs free energy
H	enthalpy
ΔH_c	heat of combustion
ΔH_{cl}	heat of combustion with initial reactant as liquid
ΔH_{clw}	heat of combustion with final water product as liquid
ΔH_{cv}	heat of combustion with initial reactant as vapour
ΔH_{cvw}	heat of combustion with final water product as vapour
ΔH_v	latent heat of vaporization
ΔH_{vw}	latent heat of vaporization of water
n	number of mols
P	absolute pressure
R	universal gas constant
S	entropy
T	absolute temperature
V	volume
W	work
γ	ratio of gas specific heats

Superscript:

o	standard state

Subscripts:

f	formation
p	products
r	reactants
1	initial state
2	final state

Section 17.4.3

U_l	liquid strain energy
V	volume of vessel
β	bulk modulus of liquid

Section 17.4.4

E	Young's modulus
K	diameter ratio
U_m	metal strain energy
V	volume of vessel
ν	Poisson's ratio

Section 17.4.5

E	internal energy
V	volume of vessel
γ	ratio of gas specific heats

Subscripts:

AG	Aslanov–Golinsky
Ba	Baker
Br	Brode
ex	explosion
Ki	Kinney
o	atmospheric

Equation 17.4.34:

R_o	scaling radius (m)

Equation 17.4.35:

E	explosion energy (te of TNT)
P_o	pressure of surroundings (kPa)
P_1	initial pressure in vessel (kPa)
V	volume of vessel (m^2)

Section 17.4.6

e	specific internal energy
E_{ex}	energy of explosion
h	specific enthalpy
p	absolute pressure
s	specific entropy
v	specific volume
x	wetness of vapour
ϕ	dummy variable

Subscripts:

f	saturated liquid
g	saturated vapour
o	atmospheric

Section 17.4.8

E_s	total energy in system
E_1	chemical energy
E_2	fluid expansion energy
E_3	vessel strain energy

Section 17.4.11

B	batch availability (kcal/mol)
δB	batch availability correction term (kcal/mol)
C_p	specific heat at constant pressure (kcal/mol)
m	number of species
P	absolute pressure (Pa)
R	universal gas constant (kcal/mol K)
T	absolute temperature (K)
x	mol fraction
ϕ_o	standard batch availability (kcal/mol)

Subscripts:

a	ambient
i	species i
pr	products
r	reactants

Section 17.5

E	expansion ratio

M	molecular weight
n	number of mols
P	absolute pressure

Subscripts:

b	bursting
1	initial
2	final

Section 17.5.4

P_{ex}	absolute explosion pressure
v_d	displacement velocity
v_{ex}	explosion velocity
v_n	normal burning velocity
ϕ	ratio of area of flame front to cross-sectional area of pipe

Section 17.6

P	absolute pressure

Subscripts:

1	initial
2	final

Section 17.7

a	radius of spherical vessel
A_f	area of flame front
C_n	calorific value of gas mixture
E	expansion ratio
F	constant
G_1–G_4	constants
h	enthalpy
k_1–k_4	constants
K	constant
K_G	constant
K_1	constant
L	length of cylinder
m	mass of gas
m_o	mass of gas in vessel
M	molecular weight
$\bar{M}$	mean molecular weight
n	fractional degree of combustion
n	(with subscript) moles of gas
P	absolute pressure
ΔP	pressure rise
Q	heat lost from burned products
r	radius
r_b	radius of burnt core of gas (after combustion)
r_c	radius of cylinder
r_i	radius of burnt core of gas (before ignition)
R	universal gas constant
R_g	mass basis gas constant
S	surface area of vessel
S_f	flame speed
S_u	burning velocity
T_{bP}	absolute temperature corresponding to pressure P
u	velocity
u_u	velocity of unburnt gas into flame front
U	internal energy
v	mass specific volume
V	volume
V_o	volume of vessel
α	coefficient of turbulence
ν	molar specific volume
ρ	mass density

Superscript:

–	normalized

Subscripts:

b	burned
e	end value (after combustion)
i	initial state of burned gas (before ignition)
j	gas state j
m	maximum
o	initial value (before ignition)
u	unburned
1	unburned
2	burned

Equations 17.7.72–17.7.78:

α	flame area factor

Equations 17.7.131–17.7.171:

a	$=1/\gamma_u$
r_s	radius of spherical vessel; radius of burned gas at end of spherical stage
α	parameter defined by Equations 17.7.143–17.7.145

Section 17.8

C	volumetric concentration
C_i	effective inlet volumetric concentration
C_o	concentration on cessation of release
Q	total volumetric flow
Q_a	volumetric flow of air
Q_g	volumetric flow of contaminant gas
V	volume of space
τ	volume/throughput ratio, or time constant

Section 17.8.7

a	index
K	constant
p	peak pressure (bar)
Q	mass of explosive (kg)
V	volume of chamber (m^3)

Section 17.10

c	volumetric concentration of component
E	number of changes of atmosphere
Q	volumetric flow of gas through vessel

Subscript:

o	initial value

Equation 17.10.4:

D	diameter of jet orifice (ft)
K	constant
V_o	nozzle velocity (ft/min)
V_x	required velocity (ft/min)
X	distance from jet to most remote corner (ft)

Section 17.11

Section 17.11.5

D	internal diameter of pipe (m)
g_L	laminar velocity gradient (s^{-1})
u_T	turbulent flashback velocity

Section 17.11.7

a	fractional free area of arrester
d	diameter of arrester apertures (cm)
n	number of apertures per unit area of arrester surface (cm^{-2})
p	explosion pressure at arrester
p_o	atmospheric pressure
V	flame speed at arrester (m/s)
y	thickness of arrester elements (cm)

Section 17.11.9

a	fractional free area of arrester
d	diameter of arrester apertures (in.)
V	flame speed at arrester (ft/s)
y	thickness of arrester (in)

Equation 17.11.6:

Q	heat of detonation of gas mixture (cal/g)
V	detonation velocity (ft/s)
γ	ratio of specific heats of gas mixture at combustion temperature

Section 17.12
(See text for units in particular equations)

a–d	constants
A, B	constants (Equation 17.12.11)
A, B, C	constants (Equation 17.12.31)
A_c	cross-sectional area of volume vented
A_m	maximum area of flame front
A_v	vent area
ΔA_v	correction term for A_v
C	Runes constant
C_d	coefficient of discharge
E	expansion ratio, expansion factor
f	vent ratio
g	acceleration due to gravity
k	constant
K	vent coefficient
K_G	K_G value
L	length of enclosure
L_1, L_2	two smallest dimensions of enclosure
m	mass of gas
$\bar{M}$	mean molecular weight
n	(with subscript) moles of gas
P	pressure
ΔP	vented explosion pressure
P_a	atmospheric pressure
P_I	back pressure due to the inertia of the vent
P_m	final pressure
P_{max}	maximum pressure in an unvented explosion
P_{red}	actual, or reduced, pressure in a vented explosion
P_{stat}	vent opening pressure
P_v	vent opening pressure
P_1	pressure of first peak
P_2	pressure of second peak
Q_m	rate of volume production
Q_v	volumetric vent outflow
r_b	radius of burned gas
R	universal gas constant
S_u	burning velocity
V	volume of vessel; volume of gas
V_f	flame speed
w	inertia of vent
W_v	mass of vent cover
Y	constant
α	coefficient of turbulemce
ρ	density of gas
ψ	vent ratio

Subscripts:

b	burned
e	vented
f	flame
o	initial
Pred	pressure in vented enclosure
u	unburned
v	vent conditions

Section 17.12.4

c	speed of sound
D	duct diameter
f_a	frequency of oscillation
f_H	frequency of Helmholtz oscillation
L	length of duct
r_s	radius of spherical vessel
α	correction factor
λ_1	constant

Section 17.12.7

f	turbulence factor

Section 17.12.10

T	absolute temperature of burnt gas

Section 17.12.20

f_v	vent outflow parameter
f_{v1}–f_{v4}	vent outflow parameters
f_{vs1}	vent outflow parameter for sonic flow
f_{vsb2}	vent outflow parameter for subsonic flow
G_v	vent mass velocity
P	absolute pressure
P_a	absolute atmospheric pressure
w	pressure ratio
w_c	critical pressure ratio
ρ_o	density of gas at atmospheric pressure

Section 17.12.21

a	radius of spherical vessel
W	mass rate of combustion

Section 17.12.22

a	characteristic length (for a sphere, the radius)
G	venting area parameter
ΔP_m	maximum explosion pressure
α	venting parameter

ρ_{bo}	density of burned gas at initial pressure
ρ_{uo}	density of unburned gas at initial pressure
χ	turbulence correction factor

Section 17.12.23

a	velocity of sound
$\bar{A}$	vent area ratio
A_s	surface area of spherical vessel
A_v	vent area
C_d	coefficient of discharge
f_{v2}	vent outflow parameter
m_v	mass vented
P	absolute pressure
S	burning velocity
$\bar{S}$	dimensionless burning velocity at vent conditions
$\bar{S}_o$	dimensionless burning velocity at initial conditions
V_v	volume vented
ζ	vent flow coefficient
ρ	density of gas

Superscript:

–	dimensionless

Subscripts:

b	burned
o	initial
u	unburned
v	vent conditions

Section 17.12.24

A_F	largest spherical surface in enclosure
A_S	surface area of sphere having same volume as enclosure
A_v	vent area
E	expansion ratio
F	shape factor
K	parameter defined by Equation 17.12.100
P	absolute pressure
ΔP	pressure difference
P_{max}	absolute maximum pressure of unvented explosion
P_o	absolute initial pressure
P_{red}	reduced pressure (gauge)
Q_v	volumetric vent outflow
r	radius of burned gas before expansion
u	velocity of flame front
V	volume of sphere
V_f	final volume of burned gas after combustion
V_{fl}	time dependent volume of fuel consumed, of burned gas before combustion
V_t	time dependent volume of burned gas after combustion

Section 17.12.25

A	area of flame front (ft^2)
A_v	vent area (ft^2)
k_{v1}	vent outflow constant (mol in. $^\circ R/lb^{\frac{1}{2}}$ ft^2 s)
k_{v2}	vent outflow constant (mol $in.^2$ $^\circ R^{\frac{1}{2}}$/lb ft^2 s)
L	length of cylinder (ft)
n	number of mols (lb mol)
P	absolute pressure ($lb_f/in.^2$)
P_m	absolute maximum pressure of unvented explosion ($lb_f/in.^2$)
P_o	atmosphere pressure ($lb_f/in.^2$)
P_{red}	absolute reduced pressure ($lb_f/in.^2$)
ΔP_v	overpressure at which vent opens ($lb_f/in.^2$)
R	gas constant (lb $ft^2/in.^2$ mol $^\circ R$)
S	burning velocity (ft/s)
t	time (s)
T	absolute temperature ($^\circ R$)
V	volume (ft^3)
α	coefficient of turbulence

Subscripts:

b	burned
e	end of combustion
m	final
o	initial
u	unburned
1	closed end side
2	vent end side

Section 17.12.26

$\bar{A}$	dimensionless vent area
A_f	area of flame front (m^2)
A_s	surface area of sphere (m^2)
A_v	vent area (m^2)
A_x	cross-sectional area of cylinder (m^2)
k	constant
n	index
ΔP_m	maximum pressure rise (atm)
r_c	radius of cylinder (m)
r_s	radius of sphere (m)
$\bar{S}_o$	dimensionless burning velocity at initial conditions
T_f	adiabatic flame temperature (K)
ρ	density of gas (kg/m^3)

Subscripts:

b	burned
o	initial
u	unburned

Section 17.12.27

A_v	vent area
B	dimensionless burning number
C_d	coefficient of discharge
G_v	vent mass velocity
m	mass
P	absolute pressure
P_a	atmospheric pressure
P_f	absolute final pressure of vented explosion, reduced pressure
P_{max}	absolute maximum pressure of unvented explosion
P_o	absolute initial pressure
P_{set}	absolute vent opening pressure
r_b	radius of burned gas
S_u	burning velocity
V	volume of vessel
Z	dimensionless burned volume

λ	dimensionless vent opening pressure
ρ	density of gas
ϕ	turbulence correction factor

Subscripts:

b	banned
e	outflow
o	initial
u	unburned

Section 17.12.28

As Section 17.7.5

Section 17.12.32

A_v	vent area
F_r	force due to back reaction
P_{red}	reduced pressure (gauge)
u	velocity of fluid
ρ	density of fluid

Section 17.12.36

a	acceleration of vent panel
A	area of vent panel
C	parameter defined by Equation 17.12.163
D	'density' of vent panel
E	parameter defined by Equation 17.12.165
F	force on vent panel
g	acceleration due to gravity
K	parameter defined by Equation 17.12.100
L	length of vent panel
M	mass of vent panel
P	pressure (gauge)
P_v	vent opening pressure (gauge)
s	distance travelled by vent panel
S	distance defined by Equation 17.12.158
t_v	time of start of venting
v	velocity of vent panel
w	vent inertia
W	width of vent panel
θ	angle of rotation of vent panel

Section 17.12

A_v/V	vent ratio
D	diameter of duct (ft)
k_1–k_4	constants
K	vent coefficient
K_{st}	dust K_{st} value
L	length of duct (ft)
L_1	distance between relief openings (ft)
L_{1max}	maximum distance between relief openings (ft)
L_2	distance between relief openings for gas other than propane (ft)
P	maximum pressure ($lb_f/in.^2$)
P_1	maximum pressure resulting from explosion of propane ($lb_f/in.^2$)
P_2	maximum pressure for gas other than propane ($lb_f/in.^2$)
S_u	maximum fundamental burning velocity for gas other than propane (ft/s)

Equations 17.3.5–17.13.6:

L	maximum distance between vents
P_{red}	reduced pressure
S	maximum fundamental burning velocity

Subscripts:

p	propane
x	gas other than propane

Section 17.14

Section 17.14.4

A_c	smallest cross-sectional area of building space (m^2)
A_v	total area of combustion vents (m^2)
f	turbulence factor
K	venting ratio
P_I	back pressure due to inertia of vent (gauge (kPa)
P_{red}	maximum pressure reached during venting, reduced pressure (gauge) (kPa)
P_v	pressure with building space at which vent opens (gauge) (kPa)
S_u	maximum fundamental burning velocity (m/s)
V	volume of enclosure (m^3)
w	vent inertia (kg/m^2)

Section 17.14.5

Equations 17.4.1–17.14.6:

A_v	vent area (ft^2)
C	Runes constant ($((lb_f/in.^2)^{\frac{1}{2}})$)
E	expansion ratio
L_1, L_2	two smallest dimensions of building (ft)
ΔP	vented explosion overpressure ($lb_f/in.^2$)
V_f	flame speed (ft/s)
ρ	density of gas (lb/ft^3)

Equation 1.14.7:

A_v	building vent area (m^2)
C	constant
L_1, L_2	two smallest dimensions of building (m)
P	maximum internal building pressure (kPa)

Section 17.14.6

a	constant
A_s	area of side of enclosure (m^2)
A_v	vent area (m^2)
K	venting ratio
P_m	maximum pressure reached during venting (mbar)
P_v	pressure at which vent opens (mbar)
P_1	first peak pressure (mbar)
P_2	second peak pressure (mbar)
S_u	burning velocity (m/s)
V	volume of enclosure (m^3)
w	vent inertia (kg/m^2)

Section 17.14.7

A_s	internal surface area of enclosure (m^2)
A_v	vent area (m^2)
C	venting constant ($bar^{\frac{1}{2}}$)

P_{red}	maximum pressure which can be withstood by weakest structural element not intended to fail (bar)

Section 17.14.8

k_1, k_2	constants
K_1	vent coefficient for compartment 1
K_{12}	vent coefficient between compartments 1 and 2
K_2	vent coefficient for compartment 2
$(Kw)_{2av}$	average value of Kw for compartment 2
P_1	vented explosion pressure of compartment 1 (mbar)
P_2	vented explosion pressure of compartment 2 (mbar)
S_u	maximum fundamental burning velocity (m/s)
V_1	volume of compartment 1 (m^3)
V_2	volume of compartment 2 (m^3)

Sections 17.16–17.19

A	vent area (m^2)
A_o	vent area for zero overpressure (m^2)
C	specific heat of reaction mass (kJ/kg)
D	diameter of vent line (m)
D_o	diameter of vent line in bench-scale apparatus (m)
F	flow correction factor for vent line
G	mass velocity ($kg/m^2\,s$)
G_o	mass velocity in bench-scale apparatus ($kg/m^2\,s$)
h	specific enthalpy (kJ/kg)
h_{fg}	latent heat of vaporization (kJ/kg)
ΔH_r	heat of reaction (kJ/kg)
ΔH_v	latent heat of vaporization (kJ/kg)
k	constant
K	discharge coefficient
L	length of vent line (m)
m	mass in vessel (kg)
m_o	initial mass in vessel (kg)
N	non-equilibrium parameter defined by Equation (17.18.2)
P	absolute pressure (Pa)
ΔP	overpressure (Pa)
P_a	atmospheric pressure (Pa)
P_g	absolute partial pressure of gas (Pa)
P_o	absolute stagnation pressure (Pa)
P_s	absolute set pressure (Pa)
P_v	absolute partial pressure of vapour (Pa)
q	heat release rate per unit mass (kW/kg)
Q	heat release or input rate (kW)
Q_g	volumetric gas evolution rate (m^3/s)
Q_v	volumetric vapour evolution rate (m^3/s)
r	rate of reaction ($kg/m^3\,s$)
t	time (s)
Δt	time interval (s)
Δt_p	emptying time (s)
Δt_v	venting time (s)
T	absolute temperature (K)
T_o	absolute stagnation temperature (K)
ΔT	temperature rise (°C)
$(dT/dt)_s$	self-heat rate at set pressure (°C/s)
T_o	absolute stagnation temperature (K)
u	specific internal energy (kJ/kg)
v	specific volume (m^3/kg)
V	volume of vessel (m^3)
W	mass flow (kg/s)
x	mass fraction of vapour, or quality
α	void fraction
β	parameter defined by Equation 17.16.10
μ	viscosity
ρ	density (kg/m^3)
τ_t	turnaround time for temperature (s)
ω	critical flow scaling parameter

Subscripts:

a	atmospheric
d	at disengagement
ERM	equilibrium rate model
f	liquid
fg	liquid–vapour transition
g	gas or vapour
l	liquid
L	laminar
m	peak pressure
o	initial
s	set point
T	turbulent
v	vapour

Equation 17.16.6:

Δt	time interval to maximum allowable pressure (s)
ΔT	temperature difference at equilibrium between initial pressure and maximum allowable pressure (°C)

Equation 17.16.8:

ΔT	temperature rise corresponding to overpressure ΔP (°C)

Equations 17.18.2–17.18.3:

ΔP	total available pressure drop (Pa)

Equation 17.18.7:

ΔT	temperature rise corresponding to overpressure ΔP (°C)

Equation 17.19.1:

ρ	density of reaction mass (kg/m^3)

Equations 17.19.5 and 17.19.7:

α_d	void fraction at disengagement
α_o	initial void fraction

Equations 17.19.7–17.19.8:

Δt_v	time to temperature turnaround (s)

Equation 17.19.12:

Q_g	peak volumetric gas evaluation rate
Q_v	peak volumetric vapour evaluation rate

Section 17.19.10

Δt_A	measured adiabatic rise time (s)
Δt_E	measured vessel emptying time (s)

Subscripts:

LS	large scale
T	test

Section 17.20

A	vent area
A_o	vent area for zero overpressure
C	specific heat of liquid at constant volume
C_{pf}	specific heat of liquid at constant pressure
C_{pg}	specific heat of gas at constant pressure
C_{vf}	specific heat of liquid at constant volume
e	base of natural logarithms
G	mass velocity of vent flow
h	specific enthalpy
h_{fg}	latent heat of vaporization
m	mass of material in vessel
m_o	initial mass of material in vessel
P	absolute pressure
q	heat release rate per unit mass
Q	heat generation or input rate
Q_T	total heat input
R	universal gas constant
V	volume of vessel
u	specific internal energy
v	specific volume
W	mass flow from vessel
x	mass fraction of vapour, or quality
ρ	density

Subscripts:

f	liquid
fg	liquid–vapour transition
g	vapour
i	phase i
m	peak pressure or temperature
o	initial
s	relief set pressure
l	vent inlet

Section 17.21

As Section 17.20, plus

Q_g	volumetric gas generation rate at temperature and pressure in reactor during relief
ΔT	difference in saturation temperature between set pressure (as redefined) and maximum allowable pressure
α	void fraction
α_d	void fraction at disengagement
α_o	initial void fraction

Subscript:

m	mean value between set pressure (as redefined) and maximum allowable pressure

Section 17.22

C	drag coefficient
d	particle diameter (m)
g	acceleration due to gravity (m/s^2)
k	constant
u	vapour velocity (m/s)
u_d	dropout velocity (m/s)
μ	viscosity of gas (cP)
ρ_l	density of liquid (kg/m^3)
ρ_v	density of vapour (kg/m^3)

Section 17.24

a	radius of vent
A	vent area
F	flow reduction factor
g	acceleration due to gravity
h	height
h_{fg}	latent heat of vaporization
ΔP	pressure drop through vent system
P_s	set pressure
Q_T	total heat input to tank
Q_v	energy release rate
s	radius of hemisphere
u	velocity of vapour through vent
u_E	entrainment velocity
u_o	velocity up vent
u_s	velocity across hemispherical surface
u_{scr}	critical velocity across hemispherical surface
ρ_g	density of vapour
ρ_l	density of liquid
σ	surface tension

Equation 17.24.8:

R_m	mass basis gas constant

Section 17.25

c_o	velocity of sound in air
i_p	positive phase overpressure impulse, impulse
i_q	dynamic pressure impulse
i_s	scaled impulse
p	overpressure
p_a	absolute ambient pressure (ahead of shock front)
p^o	peak overpressure
$p_r{}^o$	peak reflected overpressure
p_s	scaled pressure
q	dynamic pressure
q^o	peak dynamic pressure
r	distance
t_a	arrival time
t_d	duration of positive phase, duration time
t_q	dynamic pressure duration time
u	particle velocity
U	shock velocity
W	mass of explosive
z	scaled distance
α	decay parameter
γ	ratio of specific heats of air
λ	yield factor
ρ	density of air (behind shock front)
τ	scaled time
τ_a	scaled arrival time
τ_d	scaled duration time

Subscripts:

o	reference value

Equation 17.25.5:

i_q	dynamic pressure impulse (psi ms)

R	distance (ft)
W	mass of explosive (lb)

Section 17.26

i_p	impulse (Pa s)
i_s	scaled impulse (Pa s/kg$^{\frac{1}{3}}$)
p^o	peak overpressure (Pa)
p_a	atmospheric pressure (Pa)
p_s	scaled peak overpressure
t_a	arrival time (s)
t_d	duration time (s)
W	mass of explosive (kg)
z	scaled distance (m/kg$^{\frac{1}{3}}$)
τ_a	scaled arrival time (s/kg$^{\frac{1}{3}}$)
τ_d	scaled duration time (s/kg$^{\frac{1}{3}}$)

Equations 17.26.1–17.26.2:

a, b	constants
c_i	constants
i_p	impulse (kPa ms)
p^o	peak side-on overpressure (kPa)
t_a	arrival time (ms)
t_d	duration time (ms)
U	variable defined by Equation 17.26.1
z	scaled distance (m/kg$^{\frac{1}{3}}$)
ϕ	parameter defined by Equation 17.26.2

Equations 17.26.3–17.26.5:

i_p	impulse (bar ms)
p_s	scaled peak overpressure
t_d	duration time (ms)
W	mass of explosive (kg)
z	scaled distance (m/kg$^{\frac{1}{3}}$)

Equation 17.26.6:

R	distance (m)
W	mass of explosive (kg)
z	scaled distance (m/kg$^{\frac{1}{3}}$)

Equations 17.26.7–17.26.9:

a_o	speed of sound in gas (m/s)
E_{ex}	explosion energy (J)
i_s	side-on impulse (Pa s)
$\bar{I}$	scaled side-on impulse
p^o	absolute pressure of ambient air (Pa)
p_s	absolute peak side-on overpressure (Pa)
$\bar{P}_s$	scaled peak side-on overpressure
r	distance (m)
$\bar{R}$	scaled distance

Section 17.27

a	speed of sound (m/s)
a_o	speed of sound in air (m/s)
a_1	speed of sound in compressed gas (m/s)
p_o	absolute pressure of ambient air (Pa)
p_1	absolute initial pressure of gas (Pa)
p_s	absolute peak side-on pressure (Pa)
$\bar{P}_{so}$	scaled peak side-on overpressure at $\bar{R}_o$
r_o	effective radius of equivalent hemisphere (m)
$\bar{R}_o$	scaled distance
V_1	volume of gas-filled vessel (m^3)
γ_o	ratio of specific heats of air
γ_1	ratio of specific heats of compressed gas

Subscripts:

o	ambient air
1	compressed gas in vessel

Section 17.28

R	gas constant

Section 17.28.5

$\Delta A/A$	relative increase in flame surface area
A_f	disturbed flame surface area
A_o	undisturbed flame surface area
n	number of obstacles
p	pitch
r	radius of flame front
r_o	radius for flame front at entry to obstacles
S	burning velocity
S_L	laminar burning velocity
V_f	flame front velocity
V_{f1}	flame front velocity after one obstacle
V_{fn}	flame front velocity after n obstacles
V_{fo}	flame front velocity at entry to obstacles
V_L	base value of flame front velocity
α	multiplier
ρ	gas density

Subscripts:

b	burned
u	unburned

Section 17.28.10

E_{TNT}	energy of explosion of TNT (kJ/kg)
ΔH_c	heat of combustion of hydrocarbon (kJ/kg)
W	mass of hydrocarbon (kg)
W_{TNT}	equivalent mass of TNT (kg)
α	yield factor

Section 17.28.12

E_{gas}	heat of combustion of hydrocarbon (MJ/kg)
E_{TNT}	energy of explosion of TNT (MJ/kg)
M_{gas}	mass of gas (in confined/congested region) (te)
M_{TNT}	mass of TNT (te)
R	distance (m)
V	volume of gas (in confined/congested region) (m^3)
α	yield factor

Section 17.28.16

a_o	speed of sound
M_f	flame Mach number
M_p	piston Mach number
p	absolute pressure
$\bar{p}$	dimensionless overpressure
p_o	ambient pressure
r	radial distance
u	velocity
α	expansion ratio
ρ_o	density of ambient gas
ϕ	velocity potential

Section 17.28.17

a_o	velocity of sound
A_f	effective frontal area of flame
H	height of cloud
$\dot{m}$	rate of mass addition
$\ddot{m}$	rate of change of mass addition rate
M_f	flame Mach number
M_{su}	Mach number in unburned gas
p	absolute pressure
$\bar{p}$	dimensionless overpressure
p_o	ambient pressure
$\hat{q}$	dimensionless rate of energy addition
r	characteristic radius of source region
r_f	radius of flame
r_{obs}	distance of observer from centre of cloud
S_b	flame speed
S_u	effective burning velocity
u_f	velocity of flame front
$\dot{V}$	rate of volume addition
V_b	specific volume of burned gas
V_u	specific volume of unburned gas
α	expansion ratio
ρ_o	initial density of gas

Subscript:

su	unburned gas

Section 17.28.18

a	speed of sound
F	parameter defined by Equation 17.28.37
r	radial distance
r_s	radial distance of leading shock
u	particle velocity
U_s	velocity of leading shock
X	parameter defined by Equation 17.28.39
Z	parameter defined by Equation 17.28.38

Section 17.28.19

a_o	speed of sound
K	parameter defined by Equation 17.28.47b
p	parameter defined by Equation 17.28.45a
p_i	absolute pressure in region i
r	flame radius
R	shock radius
R_o	initial value of shock radius
s	parameter defined by Equation 17.28.45b
S	flame speed
T	absolute temperature in region i
V	velocity
x	parameter defined by Equation 17.28.46a
y	parameter defined by Equation 17.28.46b
θ	parameter defined by Equation 17.28.47a
ρ_i	density in region i
τ	dimensionless time defined by Equation 17.28.47c

Subscripts:

o	undisturbed gas
1	shocked gas (shell)
2	burnt gas (core)

Section 17.28.21

a	velocity of sound in normal atmosphere
E	energy
E_e	explosive energy release
E_o	total energy release
E_u	vapour cloud energy release
ΔH_c	heat of combustion
m	mass of fuel in cloud
M	molecular weight of vapour
p	pressure
p_c	pressure at centre of explosion
r	distance from centre of blast symmetry
R	distance from centre of explosion
t_o	time of termination of rapid energy release
V	volume
ϵ	stoichiometric ratio
η	explosion efficiency
ν	flame speed

Section 17.28.22

M_{su}	Mach number with co-ordinates relative to gases moving ahead of flame front
M_w	Mach number with fixed co-ordinates

Section 17.28.23

A	constant
c_o	local velocity of sound (m/s)
E_c	energy of combustion per unit volume (J/m^3)
E_o	energy added to unburned gas during combustion process (J)
L	characteristic length (m)
n	number of mols
p	absolute pressure (Pa)
$\overline{PS}$	reduced overpressure
R	distance (m)
$\bar{R}$	reduced distance
R_g	universal gas constant (J/mol K)
R_o	radius of initial cloud (m)
R_1	radius of burned cloud
t_+	duration time (s)
$\bar{t}$	reduced time
t_b	time at which explosion process is complete (s)
T	absolute temperature (K)
$\overline{TS}$	reduced duration time
U_{sw}	velocity of shock wave (m/s)
$\bar{v}_{fl}$	average flame speed (m/s)
V	volume (m^3)
γ	ratio of specific heats of air
λ	parameter defined by Equation 17.28.57

Subscripts:

o	initial
1	final

Section 17.28.24

$C(S)$	parameter ($m/J^{\frac{1}{3}}$)
E	energy content of part of cloud within flammable range (J)
ΔH_c	heat of combustion (J/kg)
M_e	mass of fuel in cloud within flammable range (kg)

$R(S)$ radius of damage circle (m)
S degree of damage
η fraction of energy released, explosion efficiency
η_c yield factor relating to stoichiometry
η_m yield factor relating to mechanical energy

Section 17.29

Section 17.29.7
T_c absolute critical temperature (K)
T_{sl} absolute superheat limit temperature (K)

Section 17.29.11
P_b burst pressure
r vessel radius
R radius ratio
σ_u ultimate tensile strength
σ_y yield strength

Subscripts:
i inner
o outer

Section 17.30

Section 17.30.4
C mass of oil mist in air necessary to produce explosive mixture at atmospheric pressure (g/m^3)
d density of oil (g/m^3)
D diameter of pipe (m)
P absolute pressure (atm)
t thickness of oil film (m)

Section 17.30.6
As Section 17.29.7

Section 17.31

Section 17.31.4
Equations 17.31.1 and 17.31.2:
a acceleration
A amplitude
f frequency
V velocity

Equation 17.31.3:
A amplitude (in.)
d distance (ft)
E mass of explosive (lb)
K constant

Equation 17.31.4:
Q mass of explosive (kg)
R distance (m)
ϕ ϕ value

Section 17.31.5
D diameter of crater (m)
h depth of crater (m)
Q mass of explosive (kg)
V volume of crater (m^3)
Equation 17.31.8:
r radius of crater
W mass of explosive

Section 17.32

Section 17.32.1
B breadth of structure
C_D drag coefficient
H height of structure
L length of structure
p overpressure
p_a maximum value of average side and top pressure
p_b maximum value of average back face pressure
p_d drag pressure
p_e effective pressure
p_f overpressure at front face
p_r^o peak reflected overpressure
p_s stagnation pressure
q dynamic pressure
S distance through which pressure relief is obtained
t time
t_s stagnation time
U shock velocity

Sections 17.32.2 and 17.32.3
c damping factor
E_{ko} initial kinetic energy
E_{sm} maximum strain energy
f Coulomb friction force
f_n natural cyclic frequency
F applied force
F^* parameter defined by Equation 17.32.12
I impulse
k elastic constant
m mass of system
R restoring force
T time constant for force decay
T_n natural period
W_m maximum work
x displacement
x_m maximum displacement
ζ damping factor
τ natural period
ω_n natural frequency

Section 17.32.4
R resistance function
R_e maximum elastic resistance

Equations 17.32.32–17.32.34:
f_n natural cyclic frequency
k elastic constant
m mass of system
T_n natural period
ω_n natural frequency

Equation 17.32.35:
B breadth of building (ft)
H height of building (ft)

T natural period of building (s)

Equation 17.32.36:
p_m blast pressure (N/m^2)
r_e maximum elastic resistance per unit area (N/m^2)
t_e time to yield (s)
T natural period (s)

Equation 17.32.37:
x_e displacement at elastic limit
x_f displacement at failure
μ ductility ratio

Section 17.32.5
F_m maximum load
P_m maximum pressure
x_e displacement at elastic limit
x_f displacement at failure
x_m central deflection

Section 17.32.6
p^o peak overpressure (N/m^2)
Y probit

Section 17.32.6
Equation 17.32.39a:
k constant
R average circle radius for specified damage category (ft)
W mass of explosive (lb)

Equation 17.32.39b:
k constant
R average circle radius for specified damage category (m)
W mass of explosive (kg)

Section 17.33

Section 17.33.2
Equation 17.33.1a:
R_B distance for B category damage (ft)
W mass of explosive (lb)

Equation 17.33.1b:
R_B distance for B category damage (m)
W mass of explosive (kg)

Section 17.33.3
Equation 17.33.2a – as Equation 17.33.1a, Equation 17.33.2b – as Equation 17.33.1b

Section 17.33.4
R_A average circle radius for A category damage
R_B average circle radius for B category damage
$\bar{R}_B$ average circle radius defined by Equation 17.33.3
R_C average circle radius for C category damage

Section 17.33.5
Equation 17.33.4 – as Equation 17.33.1b

Section 17.33.6
I impulse
P pressure
Equation 17.33.5 – as Equation 17.33.1b plus
z' modified scaled distance ($m/kg^{\frac{1}{3}}$)

Section 17.34

Section 17.34.7
E_f energy stored in vessel per unit mass of fluid
K geometric factor
M_f mass of fluid stored
M_v mass of vessel
u velocity of fragment

Subscript:
i initial

Section 17.34.8
A mean presented area of fragment
C_D drag coefficient
m mass of fragment
t time
u velocity of fragment
u_g velocity of surrounding gas
ρ_g density of surrounding gas

Section 17.34.9
As Section 17.4.5 plus
E_k explosion energy imparted to fragments
k parameter defined by Equation 17.34.8

Section 17.34.11
a_g velocity of sound in gas
K constant
M_c mass of vessel
p pressure in vessel
p_o atmospheric pressure
R_m mass basis gas constant
T absolute temperature of gas
u velocity of fragment
V_o volume of vessel
γ ratio of gas specific heats

Sections 17.34.12 and 17.34.13
a_o speed of sound
A area of detached portion of vessel wall
F parameter defined by Equations 17.34.12 and 17.34.13
L length of cylinder
m mass per unit area of vessel wall
m_f mass of fragment
P_o atmospheric pressure
P_1 absolute initial pressure in vessel
r radius of vessel
s dimension of fragment
u velocity of fragment
$\bar{u}$ dimensionless velocity of fragment

Subscript:
i initial

Section 17.34.14
a_o speed of sound in gas at failure
$\bar{E}$ scaled energy
E_{ex} energy released in explosion
M mass of vessel
P atmospheric pressure
P_1 absolute initial pressure in vessel

Section 17.34.16
C_D drag coefficient
C_L lift coefficient

Section 17.34.17
g acceleration due to gravity
k constant
u velocity along line of flight
v velocity relative to ground
x distance in horizontal direction
y distance in vertical direction
α angle of departure
β angle of return

Subscript:
i initial

Equation 17.34.46:
a drag coefficient
k constant
v velocity of projectile (ft/s)
w mass of projectile (oz)
x distance travelled by projectile (ft)

Subscript:
i initial

Section 17.34.18
A_D drag area
A_L lift area
C_D drag coefficient
C_L lift coefficient
F_D drag force
F_L lift force
g acceleration due to gravity
M mass of fragment
R range of fragment
$\bar{R}$ dimensionless range
u velocity of fragment
$\bar{u}$ dimensionless velocity of fragment
u_o initial velocity of fragment
ρ density of air
ρ_o density of air

Section 17.34.21
F_{or} orientation factor
H height of top of sphere (m)
L effective range interval (m)
N number of fragments
N_{pen} $=N-1$
P probability
P_{ri} probability that fragment falls within effective range interval L
P_{st} probability of a strike
P_v vessel pressure (barg)
r radius of sphere (m)
R range (m)
R_{med} median range (m)
R_{pen} range of penultimate fragment (m)
W combined width of target and fragment (m)
Y probit
θ angle of descent (°)

Section 17.34.24
a projected area of body (ft^2)
A area per missile (ft^2/missile)
A_h area of hemisphere on surface of which human target is standing (ft^2)
m mass of explosive (ton)
n near field number of missiles per ton of explosive (missiles/ton)
n_e number of missiles at distance R
P probability of being struck by missile
R distance (ft)
W mass of explosive (lb)
ϕ_n correction factor

Section 17.34.25
A presented area of fragment (m^2)
C constant
d diameter of fragment (m)
K constant
m mass of fragment (kg)
n_1, n_2 indices
t thickness of barricade to just stop fragment (m)
V velocity of fragment (m/s)

Section 17.34.26
d diameter of missile (m)
D calibre density of missile (kg/m^3)
e perforation thickness (m)
G parameter defined by Equations 17.34.68–17.34.70
m mass of missile (kg)
V velocity of missile (m/s)
V_p perforation velocity (m/s)
x penetration depth (m)
ρ density of concrete (kg/m^3)
σ_c compressive strength of concrete (Pa)

Section 17.34.27
d diameter of missile (m)
e_c critical impact energy of missile (J)
h thickness of target panel (m)
u ultimate tensile strength of panel (Pa)
w width of panel (m)

Section 17.34.28
E_r energy to deform sphere in plastic region between yield and rupture (kJ)
E_v energy to deform sphere up to yield point (kJ)

Section 17.34.29

E shock wave energy (J)
P equivalent static pressure (bar)
R distance (m)

Equation (17.34.76):
V volume of enclosure (m^3)

Equations 17.34.77 and 17.34.78:
I impulse per unit area ($N\,s/m^2$)
m mass of wall per unit area (kg/m^2)
V velocity (m/s)

Equation 17.34.79:
P peak incident overpressure (bar)

Section 17.35

Section 17.35.3
F force on disc
g acceleration due to gravity
m mass of disc
x extension

Section 17.35.5
e strain
U energy adsorbed (J)
ρ density of steel (kg/m^3)
σ_y yield stress (N/m^2)

Equations 17.35.1–17.35.3:
F applied force (N)
l length of pipe stretched (m)
U energy absorbed (J)
δ elongation (m)
θ angle of bend (rad)
ϕ plastic moment (N m)

Equations 17.35.4 and 17.35.5:
L length of cut (m)
t thickness (m)

Equation 17.35.6:
e_p strain behind plastic wave front
v imparted velocity (m/s)
σ_g tensile stress (N/m^2)

Equation 17.35.7:
c velocity of elastic compression wave in steel (m/s)
v velocity of impact of missile (m/s)
σ_c compressive stress caused by impact (N/m^2)
Equation 17.35.8:
V_c volume of cavity (m^3)

Section 17.36

Section 17.36.2
B, B_B constants
m mass of nth fragment
$M(n$ cumulative mass of fragments
M_o total mass of fragments
M_{oB} modified total mass of fragments
n number of nth largest fragment
λ, λ_B constants

Section 17.36.3
D velocity of detonation
u_o initial velocity of fragments
ϕ angle between initial trajectory of fragment and axis of tube, Taylor angle

Section 17.36.4
Equation 17.36.6:
C mass of cylindrical case per unit length (lb)
E mass of charge per unit length (lb)
V_o initial velocity of fragments (ft/s)

Equations 17.36.7 and 17.36.8:
C mass of explosive (kg)
C_G Gurney velocity, Gurney constant (m/s)
ΔE internal energy per unit mass of explosive (J/kg)
M mass of cylindrical section of casing (kg)
u_o initial velocity of fragments (m/s)

Equations 17.36.9 and 17.36.10:
C_G Gurney velocity (km/s)
M average molecular weight of products of explosion
N number of moles of gas produced by explosion
Q heat of detonation (cal/g)
ρ_o explosive loading density (g/cm^3)
ϕ parameter defined by Equation 17.36.10

Section 17.36.5
Equation 17.36.11:
m mass of fragment (oz)
s distance travelled (ft)
V velocity of fragment (ft/s)
V_o velocity of fragment at commencement of air drag (ft/s)

Equation 17.36.12:
A area of fragment
k constant
V velocity of fragment
V_o velocity of fragment at commencement of air drag
W mass of fragment
x distance

Equations 17.36.13–17.36.15:
A coefficient of area
A_m mean area presented by fragment in flight (ft^2)
Q fragment volume (ft^3)
V velocity of fragment (ft/s)
V_o velocity of fragment at commencement of air drag (ft/s)
V_s velocity of sound (ft/s)
w mass of fragment (oz)
x distance (ft)

Equations 17.36.16 and 17.36.17:

a diameter of sphere or side of cube (m)
A_s effective area of fragment (m^2)
C_x drag coefficient
m mass of fragment (kg)
u velocity of fragment (m/s)
u_o initial velocity of fragment (m/s)
x distance (m)
ρ_a density of air (kg/m^3)

Section 17.36.6

As Equations 17.36.13–17.36.15, plus:
time (s)
V_v initial vertical velocity (ft/s)

Equation 17.36.23:
r safety distance (m)
W mass of explosive (kg)

Section 17.36.8

A_p projected area of exposed person (ft^2)
A_v vulnerable area (ft^2)
n number of incapacitating fragments
N average number of incapacitating fragments at distance x
p probability of being hit by one or more incapacitating fragments
q number of fragments of equivalent velocity v at distance x
r proportion of fragments of equivalent velocity v at distance x capable of causing incapacitation
v velocity of fragment (ft/s)
x distance (ft)

Section 17.38

C_D drag coefficient
i impuse (Pa s)
$\bar{i}$ scaled impulse ($Pa^{\frac{1}{2}}\,s/kg^{\frac{1}{3}}$)
m mass of body (kg)
p^o peak incident overpressure (Pa)
p_a atmospheric pressure (Pa)
$p_a{}^o$ peak applicable overpressure for lung injury (Pa)
$\bar{p}_a{}^o$ scaled peak applicable overpressure for lung injury
$p_r{}^o$ peak reflected overpressure (Pa)
q dynamic pressure (Pa)
q^o peak dynamic pressure (Pa)
Y probit

Equations 17.38.9 and 17.38.10:
S damage number

Equations 17.38.11 and 17.38.13:
J impulse (Pa s)
p incident overpressure (Pa)
t_d duration time (s)

Equations 17.38.13–17.38.16:
A projected area of body (m^2)
F force acting on body (N)
i_q dynamic pressure impulse (Pa s)
t_q dynamic pressure duration (s)
V velocity imparted to body (m/s)

Equations 17.38.17–17.38.21:
A projected area of body (ft^2)
F deceleration due to friction (ft/s^2)
L loading on body (lb_f)
M mass of body (ln)
P_e effective pressure on body ($lb_f/in.^2$)
t time (s)
V velocity of body (ft/s)
x distance travelled by body (ft)
α acceleration coefficient (ft^2/lb)

Equations 17.38.22 and 17.38.23:
L loading (N)
m mass of body (kg)
t time (s)
V velocity of displacement (m/s)
ϕ_{fr} deceleration due to friction (m/s^2)

Equations 17.38.24–17.38.30:
S injury factor

Equation 17.38.31a:
d distance for 50% casualties (ft)
d_r distance for 50% casualties for 1 kt explosion (ft)
W yield of a nuclear explosion (kiloton)

Equation 17.38.31b:
d distance for 50% casualties (m)
d_r distance for 50% casualties for a 1 kte explosion (m)
W mass of explosive (te)

Section 17.40

Section 17.40.3–17.40.5

A area of pane (m^2)
A_p presented area of fragment (m^2)
A_{mp} mean presented area of fragment (m^2)
A_{50} mean frontal area of fragment (m^2)
l length of long side of fragment (m)
m_{50} mean mass of fragment (kg)
p^*_{br} breaking pressure (kPa)
p^o peak incident overpressure (Pa)
p_e^o peak effective overpressure (Pa)
t thickness of glass, fragment (m)
V velocity of fragment (m/s)
V' velocity of fragment (ft/s)
Y probit
ρ_{gl} density of glass (kg/m^3)

Superscripts:

50 geometric mean
– (overbar) scaled

Equations 17.40.5 and 17.40.6:
A^*_{50} mean frontal area fragment (cm^2)
m mass of fragment (g)
p_e^{o*} peak effective overpressure (kPa)

Equation 17.40.8:
A_{mp} mean presented area of fragment on impact (m^2)

t thickness of glass, fragment (cm)

Equations 17.40.9–17.40.10:
p'^{o}_{e} peak effective overpressure (psi)
t' thickness of pane (in.)
V'_{50} geometric mean velocity of fragment (ft/s)
$\bar{V}'_{50}$ scaled geometric mean velocity of fragment (ft/s)

Equations 17.40.12 and 17.40.13:
t^* thickness of pane (cm)
$\bar{V}_{50}$ scaled geometric mean velocity of fragment (m/s)

Equation 17.40.14:
p^{o*}_{e} peak effective overpressure (kPa)
V average velocity of fragments (m/s)

Equation 17.40.15:
t thickness of glass, fragment (m)
V average velocity of fragments (m/s)
p^*_{br} breaking pressure (kPa)

Section 17.40.6
A presented area of fragment (m^2)
A'_{50} geometric mean frontal area of fragment (m^2)
M mass of fragment (kg)
P_e peak effective overpressure (Pa)
P_o atmospheric pressure (Pa)
P_r peak reflected overpressure (Pa)
$\bar{P}_r$ dimensionless peak reflected overpressure
P_s peak side-on overpressure (Pa)
$\bar{P}_s$ dimensionless peak side-on overpressure
t thickness of pane, fragment (m)
V_{50} geometric mean velocity of fragment (m/s)
y length of square edge of fragment (m)
ρ_{gl} density of glass (kg/m^3)

Section 17.40.7
p^{o*}_{e} peak effective overpressure (kPa)
ρ_{sd} spatial density of fragments (fragments/m^2)
ρ'_{sd} spatial density of fragments (fragments/ft^2)
$\bar{\rho}'_{sd}$ scaled spatial density of fragments

Section 17.40.9
m mass of fragment (g)
V' velocity of fragment (ft/s)
Y probit

Section 17.40.10
A presented area of missile (m^2)
C_D drag coefficient
J impulse (Pa s)
M mass of missile (kg)
V_i impact velocity (m/s)
Y probit

Section 17.40.11
A presented area of fragment (m^2)
M mass of fragment (kg)
V_{50} velocity for 50% probability of perforation (m/s)

Section 17.40.12
a smaller of two dimensions of pane (m)
A area of pane (m^2)
d thickness of pane (m)
f_{dl} dynamic load factor
f_t tensile strength of pane (Pa)
P^o peak incident overpressure (Pa)
P_{df} dynamic failure load (Pa)
P_{st} static strength of pane (Pa)
t_d duration time (s)
T natural period of vibration (s)

Section 17.41

Section 17.41.24
c index
E kinetic energy (J)
m mass of fragment (kg)
u velocity of fragment (m/s)

Section 17.41.4
b, c indices
k constant
m mass of fragment (mg)
m_r mass of reference fragment (mg)
P penetration (ft)
v equivalent velocity (ft/s)
V velocity of fragment (ft/s)

Equations 17.41.7 and 17.41.8:
m mass of fragment (kg)
u velocity of fragment (m/s)
Y probit

Section 17.42
See notation lists given in text, plus:
i body region counter

Section 17.42.2
A total mean presented area of body
A_i mean presented area of body attributable to region i

Section 17.42.3
A projected area of fragment (m^2)
m mass of fragment (kg)
u velocity of fragment (m/s)
X causative factor (J/m^2)

Section 17.42.4–17.42.5
Equation 17.42.18:
a, b constants
A projected area of fragment (cm^2)
m mass of fragment (g)
u velocity of fragment (m/s)

Equations 17.42.19–17.42.22:

A	projected area of fragment (m^2)
m	mass of fragment (kg)
u	velocity of fragment (m/s)

Section 17.44

c	concentration (g/m^3)
ES	explosion severity
IE	index of explosibility
IS	ignition sensitivity
K_G	gas explosibility constant, K_G value
K_{st}	dust explosibility constant, K_{st} value
l	lower explosive limit (g/m^3)
m_{sd}	mass concentration of solvent-contaminated dust (g/m^3)
MEC	minimum explosive concentration
MEP	maximum explosion pressure
MIE	minimum ignition energy
MIT	minimum ignition temperature
MRPR	maximum rate of pressure rise
P	absolute pressure
p_{max}	maximum explosion pressure
p_o	atmospheric pressure
p_1	small initial pressure rise
p_2	pressure defined in Figure 17.114
V	volume of vessel (m^3)
ϕ_s	mass fraction of solvent in solvent-contaminated dust

Subscripts:

d	dust
dh	dust in presence of flammable gas, hybrid
g	gas
Pc	Pittsburgh coal
sample	sample

Section 17.46

C_o	maximum permissible oxygen concentration for carbon dioxide inerting
N_o	maximum permissible oxygen concentration for nitrogen inerting

Section 17.48
(See text for units in particular equations)

Section 17.48.6

A_v	vent area
f	vent ratio
V	volume of enclosure

Section 17.48.7

A_c	area of smallest cross-section of enclosure
K	vent coefficient
L_1, L_2	two smallest dimensions of enclosure

Section 17.48.8

A_v	vent area
C_d	coefficient of discharge
K_{st}	dust explosibility constant, K_{st} value
M	molecular weight of vented gas
P	pressure
P_a	atmospheric pressure
$(dP_{ex}/dt)_{maxVL}$	maximum rate of pressure rise in unvented test vessel
$(dP_{ex}/dt)_{PredVL}$	maximum rate of pressure rise in vented test vessel
P_{red}	reduced pressure
P_{stat}	vent opening pressure
R	universal gas constant
T	absolute temperature of vented gas
V	volume of vessel
V_L	volume of test vessel

Subscripts:

red	reduced
VL	test vessel

Equations 17.48.9 and 17.48.10:

a	constant
A_v	vent area (m^2)
b, c	indices
K_{st}	dust explosibility constant, K_{st} value (bar m/s)
P_{red}	reduced pressure (barg)
P_{stat}	vent opening pressure (barg)
V	volume of vessel (m^3)

Equation 17.48.11:

a, b	constants
C	constant
d	index
P_{red}	reduced pressure (barg)
P_{stat}	vent opening pressure (barg)
V	volume of vessel (m^3)

Equation 17.48.11:

B	parameter

Section 17.48.9

t	time

Equations 17.48.13a, 17.48.14a and 17.48.14b:

A	maximum pressure in unvented explosion (psi)
K	slope of line of A vs X
R	maximum rate of pressure rise
R'	average rate of pressure rise
X	vent ratio ($ft^2/100\,ft^3$)
Y	reduced pressure in vented explosion (psi)

Equations 17.48.13b, 17.48.15a and 17.48.15b:

f	vent ratio
k_{av}	constant
k_{max}	constant
P_{red}	maximum pressure in vented explosion, reduced pressure
P_{max}	maximum pressure in unvented explosion
$(dP/dt)_{av}$	average rate of pressure rise
$(dP/dt)_{max}$	maximum rate of pressure rise
S	constant

Section 17.48.10

A_c	area of smallest cross-section of enclosure

A_v	vent area
C	Runes constant
ΔP	explosion overpressure

Section 17.48.13

K_f	constant
P	absolute pressure
P_a	atmospheric pressure
$(dP_{ex}/dt)_{Pred,V}$	maximum rate of pressure rise in vented vessel
$(dP_{ex}/dt)_{Pred,VL}$	maximum rate of pressure rise in vented test vessel
t	time
V	volume of vessel
V_L	volume of test vessel
ρ	density of gas mixture

Subscripts:

ex	closed vessel explosion
Pred	reduced pressure
V	vessel
VL	test vessel

Section 17.48.14

A_v	vent area
C_d	coefficient of discharge
G_v	mass velocity through vent
K	constant
P	absolute pressure
P_o	atmospheric pressure
P_c	absolute pressure when rate of pressure rise is at its maximum
V	volume of vessel
ρ	density of gas
ρ_c	density of unburned gas at P_o or density of combustion products at P_c
ρ_o	density of gas at atmospheric pressure

Subscripts:

av	average
c	at maximum rate of pressure rise

Section 17.48.15

A_v	vent area
F	shape factor
k	constant
K_D	explosion parameter
P	absolute pressure
P_{max}	absolute maximum explosion pressure
P_{red}	reduced pressure (gauge)
u	velocity of flame front
V	volume of vessel

Section 17.48.16

As Section 17.12.25

Section 17.51

f	number of fatalities
MI	mortality index
r	radius
W	mass of explosive

Section 17.52

Section 17.52.1

n	index
p^o	peak overpressure
r	distance
W	mass of explosive
z	scaled distance

Subscript:

r	reference value

Section 17.52.2

I	mass of vapour in cloud (te)
k^*	constant
p^o	peak overpressure (bar)
r	distance (m)
r_c	radius of cloud (m)
R_{LFL}	distance to LFL (m)

18 Toxic Release

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The third of the major hazards, after fire and explosion, is a release of a toxic chemical. The hazard presented by a toxic substance depends on the conditions of exposure and on the chemical itself. It ranges from a sudden brief exposure at high concentration to prolonged exposure at low concentrations over a working lifetime.

Both these situations present serious hazards. A very large release of a toxic chemical such as chlorine under the most unfavourable conditions is usually regarded as having a disaster potential greater than that of fire or explosion. However, a large toxic release is a much less frequent occurrence than a large fire or explosion.

The *First Report* of the ACMH (Harvey, 1976) states:

> With toxic materials, the sudden release of very large quantities could conceivably cause even larger numbers of casualties than a flammable escape. In theory such a release could, in certain weather conditions, produce lethal concentrations in places 20 miles from the point of release but the actual number of casualties (if any) would depend on the population density in the path of the cloud and the effectiveness of the emergency arrangements which might include evacuation.

In a quite different way the long-term toxic effects of exposure at even low concentrations of certain chemicals over a working lifetime can also affect large numbers of people.

The aspects of the problem considered here are the general effects of toxic substances, the limit values set for these, the effects of particular toxic chemicals and the assessment and control of the hazard of toxic releases. The treatment here is complemented by the account of occupational health given in Chapter 25.

Reference was made in Chapter 3 to the establishment by the Government of the Advisory Committees on Dangerous Substances (ACDS) and on Toxic Substances (ACTS) to advise the Health and Safety Commission. The terms of reference of both committees include toxic substances.

It cannot be too strongly emphasized that the assessment of the effect of toxic chemicals is a medical matter and that it is essential that the engineer seek expert advice on medical aspects such as interpretation of limit values and assessment of long-term effects.

Selected references on toxicology and toxic chemicals and on toxic release are given in Tables 18.1 and 18.2, respectively.

18.1 Toxic Effects

The treatment of toxic effects given here deals both with acute and chronic effects, but it is necessarily a brief one. Sources of information on the toxicity of chemicals are given in Section 18.3, and for carcinogens, in Section 18.7.

The effects of toxic substances are described in treatments of occupational diseases such as *Occupational Diseases and Industrial Medicine* (R.T. Johnson and Miller, 1960), *Diseases of Occupations* (Hunter, 1975), *National Occupational Exposure Survey* (NIOSH, 1974–/3), *Occupational Diseases – A Guide to Their Recognition* (NIOSH, 1977/4), *A Guide to Work-relatedness of Disease* (NIOSH/5, 1979), *Recognition of Health Hazards in Industry* (Burgess, 1981 ACGIH/5), *Chemical Exposure and Disease* by Sherman (1988

Table 18.1 *Selected references on toxicology and toxic chemicals*

MCA (SG–1); Anon. (1948); J.H.F. Smith (1956); Hunter (1959, 1975); H.H. Fawcett (1965f, 1982f,g); Watkins, Cackett and Hall (1968); Kinnersly (1973); Presidents Science Advisory Committee, Panel on Chemicals and Health (1973); Stellmann and Daum (1973); Gadian (1974, 1978); HSE (1977 EH 18); M.L. Miller (1977); Lippmann and Schlesinger (1979); Shapo (1979); D.J. Hughes (1980)

Toxicology, toxicity assessment
Lehmann and Flury (1938); Gilman and Cattell (1948); Patty (1948–); Hodge and Sterner (1949); Brodie (1956); Spector (1956a); Fairhall (1957); Elkins (1959); W.M. Grant (1962); Warren *et al.* (1963); E. Browning (1965); H.H. Fawcett (1965d,f); Foulger (1965); Deichman and Gerarde (1969); Sunshine (1969, 1978); Paget (1970, 1978); Wilcox (1970); Ames (1971); Havener (1971); Ames *et al.* (1973); P. Cooper (1974); Hemsworth (1974); Loomis (1974); Stolz *et al.* (1974); Casarett and Doull (1975); Hunter (1975); Blackadder (1976); J.T. Carter (1976, 1980); Plunkett (1976); Duncan (1977); Funes-Cravioto *et al.* (1977); Clayton and Clayton (1978, 1981, 1982); Food Safety Council (1978); The Royal Society (1978); M. Sherwood (1978); M.J. Wallace (1978); WHO (1978); Cralley and Cralley (1979, 1983); Patrick (1979); Eschenroeder *et al.* (1980); M. Stephenson (1980); Neuman and Benashki (1981); A.L. Reeves (1981); H.J. Rogers, Spector and Trounce (1981); Tu (1981–); Wands (1981); Anon. (1982a); Crouch and Wilson (1984); Hymes (1984); Jameson and Walters (1984); Walters and Jameson (1984); Albert (1985); Baxter (1985); Environ Corporation (1986, 1989); Klaassen, Amdar and Doull (1986); Matthiessen (1986); Klimisch *et al.* (1987); Springer (1987); ACGIH (1988/26, 1990/46); Hayes (1989); T. Robinson and Yodaiken (1989); R.M. Turner and Fairhurst (1989a); Alexeeff, Lewis and Lipsett (1992); Bosch (1992)

Toxicity testing
WHO (EHC 6); Goldberg (1974); Christopher (1978); Dewey (1978); M. Sherwood (1978); Smythe (1978); Anon. (1982a); Kolber *et al.* (1983); Patrick (1983); Rodricks and Tardiff (1984a); Walters and Jameson (1984); Anon. (1986a); ten Berge, Zwart and Appelman (1986); Kletz (1987e); ten Berge and Zwart (1989)

Epidemiology
Acheson (1967, 1979); J.P. Fox, Hall and Elvaback (1970); Lowe and Kostrzewski (1973); Tsuchiya, Okubo and Ischizu (1975); Alderson (1976); Duncan (1977, 1979); Wynder and Gori (1977); Registrar General (1978); Harrington (1979, 1980a); Lawther (1979); Monson (1980); Acheson and Gardner (1981); A.J. Fox (1981); Ryan (1981); Clary, Gibson and Waritz (1983); Leese and Jones (1983); Neal and Gibson (1984); CONCAWE (1991, 91/53); ACGIH (1992/79)

Toxic load–response
Bryan and Shimkin (1945); B.G. King (1949); J.M. Brown (1976); Liddell, McDonald and Thomas (1977); Hewitt (1978); M.W. Anderson, Hoel and Kaplan (1980); Krewski and van Ryzin (1981); Hoel, Kaplan and

Anderson (1983); C.C. Brown (1984); Ride (1984b); Snyder (1984); Anon. (1986i); ten Berge, Zwart and Appelman (1986); Zwart *et al.* (1988)

Toxicokinetic modelling
Dominguez (1933); E. Nelson (1961); J.G. Wagner (1975); Tuey (1980); Muller and Barton (1987)

Human and animal physiology
Gilman *et al.* (1948); Farris and Griffiths (1949); Spector (1956b); R.T. Williams (1959); Oser (1965); Altman and Dittmer (1961, 1968, 1971, 1974); Weibel (1963); Munro (1969); Zenz (1975); Mitruka and Rawnsley (1977); Parke and Smith (1977); J.B. West (1977); Altman and Katz (1979); Waldron (1979, 1989); Harrington and Waldron (1980); Schroter and Lever (1980); Waldron and Harrington (1980); Ganony (1983); Lindberg, Dolata and Merke (1987)

Statistical interpretation
Trevan (1927); Bliss (1934, 1935, 1952, 1957); Bliss and Cattell (1943); Finney (1971)

Animal models, extrapolation between species
Freirech *et al.* (1966); Rall (1970); S.B. Baker, Tripod and Jacob (1970); Hushon and Ghovanlou (1980); Paddle (1980); Purchase (1980); Oser (1981); Task Force of Past Presidents of the Society of Toxicology (1982); C.C. Brown (1984); Menzel and Smolko (1984); N. Nelson (1984); Rousseaux (1987)

Toxic risk assessment
NAS/NRC (1973b); Zeller (1979); Ruschena (1980); US Congress, OTA (1981); Totter (1982); Rodricks and Tardiff (1984b); Bridges (1985); Clayson, Krewski and Munro (1985)

Toxics control policy
Anon. (1981k); Pittom (1978); Relio (1978); C. R. Pearson (1982); Barnard (1984); Corn and Corn (1984); Deisler (1984a,b); Gough (1984); Karrh (1984); Lowrance (1984); Neal and Gibson (1984); Rijkels (1984); Rodricks and Tardiff (1984); Doull (1987); Rodricks and Taylor (1989); Cote and Wells (1991); Fairhurst and Turner (1993)

Process design and handling
Halley (1965); Prugh (1967); J.R. Hughes (1970); Constance (1971a); Gage (1972); Schaper (1973); Kusnetz (1974); Wirth (1975); J.T. Carter (1976, 1980); Garner (1976); Weissbach (1976); Toca (1977); Payne (1978); S.D. Green (1980); IBC (1982/27); Cralley and Cralley (1983); First (1983); Kusnetz and Phillips (1983); Kusnetz and Lynch (1984); Carson and Mumford (1986 LPB 67); Anon. (1989 LPB 86, p. 19); Jackson (1989 LPB 87); Desai and Buonicore (1990); Grossel (1990a); Doerr and Hessian (1991); Chadha and Parmele (1993)

Workplace exposure, environmental control, exposure monitoring; analytical methods (*see* Table 25.1)

Toxics detection and alarm
D. Doyle (1971); ACGIH (1972); Eckstrom (1973); Blears and Coventry (1974); Johanson (1974, 1976); Visanuvinol and Slater (1974); Dailey (1976); Thain (1976); Lichtenberg and McKerlie (1979); Warncke (1977); Ricci (1979a); Ellgehausen (1980); Cullis and Firth (1981); Rooney (1986); J.M. Rogers (1988); Thompson, Sekula and Whitson (1992)

Hygiene standards, threshold limit values, occupational exposure limits
ACGIH (n.d./1–3, 1992/78, 80); Elkins (1939); Bowditch *et al.* (1940); Anon. (1962a); Associated Octel Co. (1972 Bull. 24); ASTM (1973 DS 48); Levinson (1975); Ferguson (1976); HSE (1976 TDN2/73, 1993, EH 64, EH 65/4, EH 65/6, 1994 EH 40); Henschler (1979); Lauwerys (1983); IBC (1984/56); CIA (1985 PA23); P. Lewis (1985a, 1986a,b); Skinner (1985); AIHA (1987/12); Anon (1990h); ILO (1991/2); Weisburger (1994)
MAKWerte: Henschler (1979); Deutsche Forschungsgemeinschaft (1982); German Commission for Investigation of Health Hazards in the Workplace (1994)
Emergency exposure limits: Zielhuis (1970); Siccama (1973); CPD (1974); Balemans (1975); Eisenberg, Lynch and Breeding (1975); AIHA (1988–/13); ECIETOC (1991); Rusch (1993)
HSE limit system: Fairhurst and Turner (1993)
Dow Chemical Exposure Index: R.A. Smith and Miller (1988); Dow Chemical Co. (1994a)

Odour
(ASTM 164, 1973 DS 48); Leonardos, Kendall and Barnard (1969); Turk (1969); ASTM (1973 DS 48); Turk, Johnston and Moulton (1974); Cheremisinoff and Young (1975); Fazzalari (1978); Eugen (1982); Polak (1983); Lynskey (1984 LPB 60); J.C. Stevens, Cain and Weinstein (1987); AIHA (1989/17)CCPS (1989/4); R.M. Turner and Fairhurst (1989a); MacFarlane and Ewing (1990); ACDS (1991); de Weger, Pietersen and Reuzel (1991); CPD (1992b)

Toxicity of chemicals
Browning (n.d.a,b, 1965); HSE (Appendix 28 inc. *Toxicology of Substances*, MS, TDN and TR series, SIR 21); MCA (1952– SD series, 1972/21); Merck (1889); Flury and Zernick (1931); Brookes (1948); Patty (1948–); Sax (1957–); Matheson Co. (1961); C.H. Gray (1966); BCISC (1968/8); Skinner (1962); Braker and Mossman (1970); G.D. Muir (1971); Kinnersly (1973); National Library of Medicine (1974); Sumi and Tsuchiya (1976); Binns (1978); Skole (1978); Sittig (1979, 1981, 1994); Deutsch (1981); CONCAWE (1984 84/54, 1986 86/69); A. Allen (1988); Walsh (1988); van Loo amd Opschoor (1989); Merck Co. (1989); Meyer (1989); NIOSH (1990/18); Franklin (1991); OSHA (1991/7); Kellard (1993); Tyler *et al.* (1994)

Carcinogens
HSE (TDN series, 1973 TDN 3, 1983 MS(B) 5); OSHA (n.d./2, OSHA 2220, 1977); Public Health Service (1941–); Bryan and Shimkin (1945); MCA (1952– SD series); Hunter (1959, 1975); Mantel and Bryan (1961); Munn (1963); Surgeon Generals Advisory Committee on Smoking and Health (1964); J.A. Miller (1970); Ames (1971); J.G. Wilson (1971); Ad Hoc Committee on the Evaluation of Low Levels of Environmental Carcinogens (1972); Gadian (1972); IARC (1972–, 1979a, 1980); Abelson (1973); Ames *et al.* (1973); Hollaender (1973); Goldberg (1974); Ricci (1974, 1976a,b, 1977a); T'so and di Paulo (1974); Cairns (1975, 1981); R.L. Carter and Roe

(1975); Environmental Mutagen Society (1975); Fraumeni (1975); Hoover and Fraumeni (1975); McCann *et al.* (1975–); Cinkotai *et al.* (1976); A.J. Fox and Collier (1976); Mehlman, Shapiro and Blumenthal (1976); Searle (1976–); Baxter *et al.* (1977); Boyland (1977); Doll (1977, 1979); Kraybill and Mehlman (1977); Schirripa (1977); Wynder and Gori (1977); Ashby and Styles (1978); S.S. Epstein (1978); Rawson (1978); Tarr and Damme (1978); Bowman (1979, 1982); B.E. Butterworth (1979); Doll and McLean (1979); Fairchild (1979); Fishbein (1979); Garner (1979); Grasso (1979); Higginson and Muir (1979); OSTP (1979); Peto (1979, 1980); P.P. Scott (1979); Sullivan and Barlow (1979, 1982); Vogel (1979); M.W. Anderson, Hoel and Kaplan (1980); ASTM (1980); Purchase (1980); Cairns (1981); CIA (1981, 1992 RC45); Doll and Peto (1981); S.E. Epstein and Swartz (1981); IBC (1981/14); A.E. M. McLean (1981); Sax (1981); C.R. Shaw (1981); Sontag (1981); Squire (1981); US Congress, OTA (1981); Anon. (1982n); Magnus (1982); de Serres and Shelby (1982); Soderman (1982); Stich (1982–); Totter (1982); Bootman (1983); CBI (1983); Doyal and Epstein (1983); Hoel, Kapland and Anderson (1983); Barnard (1984); Corn and Corn (1984); Deisler (1984a,b); Gough (1984); Higginson (1984); Karrh (1984); Kirsch-Volders (1984); Kusnetz and Lynch (1984); Lowrance (1984); Neal and Gibson (1984); Rijkels (1984); Sagan and Whipple (1984); Crump and Crockett (1985); Wolf (1985); Blackburn and Kellard (1986); Anon. (1986i); CIA (1987 RC5); Tancrede *et al.* (1987); HSE (1990 EH 58, 1992 EH 62)
Benzene: Thorpe (1974, 1978a,b); NIOSH (1976 Publ. 74–137); Infante *et al.* (1977a,b); Laskin and Goldstein (1977); Kohn (1977b); Tabershaw and Lamm (1977); Pagnotto, Elkins and Brugsch (1979); Cahan (1980); Rushton and Alderson (1981); HSE (1982 TR 4); M.C. White, Infante and Chu (1982); ACGIH (1989/28); Foo (1990); HSE (1992 MS(A) 13); IP (1993 TP 25, 26)
Formaldehyde: HSE (1981 TR 2); Clary, Gibson and Waritz (1983); Starr (1983)
Vinyl choride: OSHA (OSHA 2225); Viola (1970); Schaper (1973); Anon. (1974j); HM Chief Inspector of Factories (1974); BCISC (1974/14); Creech and Johnson (1974); Anon. (1975o); CIA (1975/8); Creech and Makk (1975); EPA (1975b,c); HSE (1975b, 1992 EH 63); Heath, Falk and Creech (1975); Lilis *et al.* (1975); Maltoni and Lefemine (1975); Nicholson *et al.* (1975); Selikoff and Hammond (1975); Veltman *et al.* (1975); Baxter *et al.* (1977); H.M. Clayton (1977); Meade and Press (1977); Stafford (1977); Tarpa (1977); Atherley (1978); Doniger (1978); Gehring, Watanabe and Park (1979); McPherson, Starks and Fryar (1979); Anon. (1980x); Conaway, Davenport and Norstrom (1980); Anon. (1984z); Rijkels (1984); Barr (1986); Wolf, Holland Rajaratnam (1987)

Dusts
HSE (TDN 14, 1976 TDN 1, 1979 EH 21, 1990 EH 46, 1991 EH 44, 1992 EH 59, 1993 EH 66, 1994 CRR 62); Stairmand (1951); C.N. Davies (1954); Bamford (1961); Owen (1974); T. Allen (1975); Batel (1976); Munns (1977); Kaye (1981); Vincent and Marks (1981); Bridgwater (1983); Orleman *et al.* (1983); Sexton, Spengler and Treitman (1984); BOHS (1985 TG5, 1987 TG7); D.M. Muir (1985); ACGIH (1987/13, 1988/18); Lloyd (1987); Mody and Jakhete (1988); Rood (1992a,b); Stanley-Wood and Lines (1992)
Silica dusts: HSE (1992 MS(A) 15)
Organic dusts: HSE (1977 MS 4); VDI 2263 Pt 1: 1990
Asbestos: HSE (Appendix 28 *Asbestos*, MA 4, TDN 42, 1970 HSW Bklt 44, 1974 TDN 13, 1975 TDN 24, 35, 1982 RP 18, 1984 IND(G) 17(L), 1985 EH 41, 1986 Research Review 3, 1988 EH 50, MS 13, 1989 EH 35, 37, 51, 1990 EH 10, 36, 47, 1993 EH 57); Oliver (1902); Doll (1955); J.C. Wagner (1960); Gadian (1967); Elmes and Simpson (1971, 1977); Langlands, Wallace and Simpson (1971); Wallace and Langlands (1971); DoEm (1974/4); Parliamentary Commissioner (1975–76); Edge (1976); Fulmer Research Institute (1976); Harries (1976); W.P. Howard (1976); Kinnersly (1976); Lumley (1976); D.C.F. Muir (1976); Selikoff, Churg and Hammond (1976); Tait (1976); European Commission (1977); NIOSH (1977 Crit. Doc. 77–169); Woolf (1977); Cavaseno (1978c); HSC (1978a,b); Peto (1978); Savage (1978); British Society for Social Responsibility in Science (1979); Pye (1979); Carton and Kauffer (1980); Gee (1980); J.W. Hill (1980); Basta (1981a); Gentry *et al.* (1982); T. Nash (1982); ASTM (1984 STP 834); J.Bell (1984); Ouellette *et al.* (1986); WHO (1986 EHC 53); Holt (1987); ACGIH (1989/33, 1990/39)
Dust–fume mixtures: HSE (1994a)
Welding fumes: AWS (Appendix 28); Welding Institute (1981/35, 36, 1986/38, 1991/43); HSE (1990 EH 54, EH 55)

Aerosols
C.N. Davies (1961, 1967); Vincent (1980); Hinds (1982)

Metals
HSE (Appendix 28 EH series, *Technical Data Notes*); A. Tucker (1972); Goyer and Mehlman (1977); A. Williams (1977); Cohn and Linnecar (1979)
Arsenic: HSE (TDN 9, 1990 EH 8); Lederer and Fensterheim (1983); OSHA (1983)
Cadmium: HSE (1975 TDN 11, 1986 EH 1, MS(A) 7); Mennear (1979)
Chromium: HSE (1991 EH 2, MS(A) 16)
Lead, lead additives: API (69–7, EA 7102); HSE (TDN 16, EH 3, MA 3, 1986 BPM 16, EH 28, MS(A) 1); OSHA (OSHA 2230); WHO (EHC 3); Cremer (1959, 1961); Cremer and Callaway (1961); R.K. Davis *et al.* (1963); Bryce-Smith (1971, 1982); Hepple (1971); Associated Octel Co. (1972 Bull.24); NAS/NRC (1972b); DoEm (1973/3); Gething (1975); HSE (1978b); NIOSH (1978 Crit. Doc. 78–158); Anon. (1982d); Chamberlain (1983); Killington (1983); E. King (1983); ACGIH (1991/75); Sweetland (1993)
Mercury, including methyl mercury: WHO (EHC 1); OSHA (OSHA 2234); Katsuna (1968); Hartung and Dinman (1972); Bakir *et al.* (1973); OECD (1974); HSE (1978 MS 12); D. Taylor (1978); P.R. Edwards and Pumphrey (1982)

Inhalation toxicity
Barcroft (1918, 1920); Waldron (1980a); Hardy and Collins (1981); Witschi and Nettesheim (1981–); Fiserova-Bergerova (1983); ASTM (1985 STP 872)
Respiratory physiology: Krogh (1914–15); Forbes, Sargent and Roughton (1945); Forster (1957, 1964a,b); Ogilvie *et al.* (1957); Weibel (1963, 1973); Fenn and Rahn (1964); J.B. West (1965, 1977); Lippold (1968); Altman and Dittmar (1971, 1974); Comroe (1974); Lambertsen (1974); Mountcastle (1974); Cotes (1979); Pickrell (1981);

Keele, Neil and Joels (1982); Bramble (1983); Whipp and Wiberg (1983); Phalen (1984); Nixon (1985, SRDR 327); Vouk *et al.* (1985)

Lung diseases
Parkes (1974); C.K.W.M. Morgan and Seaton (1975); HSE (1977 MS 5); Khogali (1977)

Toxic gases
McEwen, Theodore and Vernot (1970); McEwen and Vernot (1972, 1974, 1976); Perry and Articola (1980); Buckley *et al.* (1984); CCPS (1989/4); R.M. Turner and Fairhurst (1989a); MacFarlane and Ewing (1990); ACDS (1991); de Weger, Pietersen and Reuzel (1991); CPD (1992b)
Gas warfare, war gases: Hendry and Horsburgh (1915); R. Parker (1915a,b); Sieur (1915); Wainwright (1915); Haldane (1917, 1919, 1925); Chemical Warfare Medical Committee (1918–); Edkins and Tweedy (1918); Hunt and Price Jones (1918); Parsons (1918); Baskerville (1919); Carr (1919); Lidbetter and Monk-Jones (1919); Kerschbaum (1920); Tatham and Miles (1920); Lefebure (1921, 1928); Winternitz, Smith and McNamara (1920); Winternitz *et al.* (1920); Oudry (1924); Serrant (1924); Vedder (1925); Walton (1925); Le Wita (1925); Bloch (1926); Bressou (1926); Sesselberg (1926); von Deimling (1931); Hanslian (1931, 1934); T.J. Mitchell and Smith (1931); Abbott (1933); Dautrebaude (1933); Fessler, Gebele and Prandtl (1933); Leroux (1933); Mordaq (1933); Zernik (1933); Heeressanitätsinspektion (1934); von Tschischwitz *et al.* (1934); Ferry (1935); Noskoff (1935); Prentiss (1937); Gerchik (1939); National ARP Animal Cttee (1939); G.W. Young (1953); D.K. Clark (1959); McNalty and Mellor (1968); Haber (1975, 1986); McWilliams and Steel (1985); Finch (1986); Withers and Lees (1987b); R.F. Griffiths and Fryer (1988); Butcher (1989a); V.C. Marshall (1989b); Lees and Withers (1992)
Aerosols: C.N. Davies (1961, 1966, 1967); Walton (1971, 1977)
Acrylonitrile: Dudley and Neal (1942); Dudley, Sweeney and Miller (1942); Ministry of Social Affairs (1972); Solomon, Rubin and Okrent (1976); Bochinski, Schoultz and Gideon (1979); HSE (1981 EH 27); EPA (1983); WHO (1983 ECH 28); R.M. Turner and Fairhurst (1989b)
Ammonia: Underwriters Laboratories (n.d.a); WHO (EHC 54); NIOSH (1974 Crit. Doc. 74–136); Lehmann (1886, 1899a); Hess (1911); Flury (1921a, 1928); Haggard (1924); Slot (1938); McCallan and Setterstrom (1940); Thornton and Setterstrom (1940); Weedon, Hartzell and Setterstrom (1940); Caplin (1941); Boyd, MacLachan and Perry (1944); Silver and McGrath (1948); Carpenter, Smyth and Pozzani (1949); Silverman, Whittenberger and Muller (1949); Ting (1950); Weatherby (1952); von Meythaller and Gross (1957); Derobert (1964); Gaultier (1964); Levy *et al.* (1964); Saifutdinouv (1966); Mulder and van der Zalm (1967); Niden (1968); Osmond and Tallents (1968); Zygadowski (1968); McGuiness (1969); Coon *et al.* (1970); Voison *et al.* (1970); Helmers, Top and Knapp (1971); E.S. White (1971); Kass *et al.* (1972); NAS-NRC (1972a); Pernot *et al.* (1972); Prokopeva, Yushkov and Ubasheev (1973); Slack and James (1973); Walton (1973); Eisenberg, Lynch and Breeding (1975); Prokopeva and Yushkov (1975); Taplin *et al.* (1976); Sobonya (1977); Verberk (1977); Vernot *et al.* (1977); Dalton and Bricker (1978); HSE (1978b); Hilado and Cumming (1978); Kondrasuov (1978); Richard, Bouley and Boudene (1978); Richard, Jounay and Boudene (1978); Hatton *et al.* (1979); Kane, Barrow and Alarie (1979); Alarie (1980); Montague and MacNeil (1980); Hofer, Reindle and Hruby (1981); Appelman, ten Berge and Reuzel (1982); Kapeghian *et al.* (1982); Flury *et al.* (1983); O'Kane (1983); S.K. Price *et al.* (1983); K. Ward, Murray and Costello (1983); R.F. Griffiths and Megson (1984); Arwood, Hammond and Ward (1985); Engelhardt and Holliday (1985); Lessenger (1985); WHO (1986 ECH 54); Withers (1986a); Markham (1987a,b); MHAP (1988); Pedersen and Selig (1989); Sakurai (1989); Payne, Delic and Turner (1990); Ryer-Powder (1991); Brockhoff, Petersen and Haastrup (1992)
Aniline: Anon. (LPB 30 1979, p. 165)
Bromine: Lehmann (1887, 1893); L. Hill (1915); Symes (1915a,b); Haggard (1924); Chlopin (1927–); Jolles (1966); Schlagbauer and Henschler (1967); Bitron and Aharonson (1978); Withers and Lees (1986b, 1987a); P.C. Davies and Purdy (1987)
Carbon monoxide: Lewin (1920); NIOSH (1972 Crit. Doc. 73–11000); OSHA (OSHA 2224); HSE (HSW Bklt 29, 1984 EH 43); WHO (EHC 13); Drescher (1920); API (1972 Publ. 4131); Connor (1984); Esposito and Alarie (1989); Sakurai (1989)
Carbon disulphide: WHO (EHC 10); Teissinger and Soucek (1949)
Chlorine: HSE (HSW Bklt 37); WHO (EHC 21); Lehmann (1887, 1899a,b); Anon. (1915a–g); Broadbent (1915); H. Campbell (1915); Golla and Symes (1915); Hake (1915); Klotz (1917); Anon. (1918); Anon (1919); Anon (1920); Underhill (1920); Anon. (1923); Vedder (1925); Anon. (1926); McCord (1926); Chlopin (1927–); Walton and Eldridge (1928); Anon. (1930); Anon. (1933c); David (1933a,b); Skljanskaia, Klaus and Ssidorowa (1935); Skljanskaia and Rappoport (1935); Arloing, Berthet and Viallier (1940); McCallan and Setterstrom (1940); Thornton and Setterstrom (1940); Weedon, Hartzell and Setterstrom (1940); Silver and McGrath (1942); Silver, McGrath and Ferguson (1942); Malone and Warin (1945); Tatarelli (1946); Chasis *et al.* (1947); Baader (1952); Joyner and Durel (1962); Gervais *et al.* (1965); Kowitz *et al.* (1967); C.G. Kramer (1967); Schlagbauer and Henschler (1967); Dixon and Drew (1968); Krause, Chester and Gillespie (1968); Capodaglio *et al.* (1969); Stahl (1969a); Weill *et al.* (1969); Patil *et al.* (1970); Sessa *et al.* (1970); Urogoda (1970); Zielhuis (1970); Adelson and Kaufman (1971); Leube and Kreiter (1971); NAS-NRC (1973a, 1976); BCISC (1975/1); Eisenberg, Lynch and Breeding (1975); T.B. McMullen (1975); Ministry of Social Affairs (1975); NIOSH (1976 Crit. Doc. 76–170); Schwartz (1976); Solomon, Rubin and Okrent (1976); Barrow *et al.* (1977); Bitron and Aharonson (1978); HSE (1978b); Dewhirst (1981a–c); Anon. (1984f); Chlorine Institute (1985 Publ. 63); P. Davies and Hymes (1985); Dokter *et al.* (1985); McWilliams and Steel (1985); MHAP (1985 LPB 64, 1987); Withers (1985, 1988); Withers and Lees (1985a,b, 1987b, 1992); Nussey, Mercer and Fitzpatrick (1986); R.F. Griffiths and Fryer (1988); Holton and Montague (1988); Zwart and Woutersen (1988); CIA, Chlorine Sector Group (1989); V.C. Marshall (1989b, 1990a); Sakurai (1989); R.M. Turner and Fairhurst (1990a); Brockhoff, Petersen and Haastrup (1992); Anon. (1993 LPB 113, p. 26)

Dimethylformamide: Bauer (1980)
Ethylene dichloride: Heppel *et al.* (1946)
Ethylene oxide: CISHC (1975/2); NIOSH (1978 Crit. Doc., 77–200); CIA (1979 RC 14); Flores (1983); Desai and Buonicore (1990)
Halogenated hydrocarbons: Lehmann and Schmidt-Kelh (1936); von Oettingen (1937)
Hydrogen chloride: WHO (ECH 21); Lehmann (1886); Leites (1929); Machle *et al.* (1942); Elfimova (1959, 1964); Jacobziner and Raybin (1962); Stahl (1969b,c); Nagoa *et al.* (1972); Hilado and Furst (1976); NAS/NRC (1976); Barrow *et al.* (1977); Hilado and Cumming (1978); Barrow, Lucia and Alarie (1979); Alarie (1980)
Hydrogen cyanide: Geppert (1889); Hess (1911); Flury and Heubner (1919); Fühner (1919); Drescher (1920); Koelsch (1920); Reed (1920); Hasselmann (1925a,b); Chlopin (1927–); Schütze (1927); Dschang (1928); Flury (1928); Walton and Witherspoon (1928); Schwab (1929); Barcroft (1931); Hug (1932); Wirth and Lammerhirt (1934); Wirth (1935, 1937); Prentiss (1937); Kendall (1938); McCallan and Setterstrom (1940); Thornton and Setterstrom (1940); Weedon, Hartzell and Setterstrom (1940); Wachtel (1941); Waitt (1942); Wood (1944); British Intelligence Objective Subcommittee (1946); Brophy, Miles and Cochrane (1959); Hilado and Furst (1976); McNamara (1976); NIOSH (1977 Crit. Doc. 77–108); Vernot *et al.* (1977); Hilado and Cumming (1978); Ride (1984a); Holton and Montague (1988); Esposito and Alarie (1989); Sakurai (1989)
Hydrogen fluoride: Ronzani (1909); Muehlberger (1928); Simons (1931); Machle *et al.* (1934); Machle and Kitzmiller (1935); Machle and Scott (1935); Stokinger (1949); Rushmere (1954); Rosenholtz *et al.* (1963); McEwen and Vernot (1970); Darmer, Haun and MacEwan (1972); Hilado and Furst (1976); NIOSH (1976 Crit. Doc. 76–143); Vernot *et al.* (1977); CIA (1978); Hilado and Cumming (1978); Valentine (1988); Mudan (1989a); HSE (1990 MS(A) 12); R.M. Turner and Fairhurst (1990b)
Hydrogen sulphide: Biefel and Poleck (1880); Lehmann (1892, 1893, 1899a); Haldane (1896); Hess (1911); Haggard and Henderson (1922); Sayers, Mitchell and Yant (1923 BM RI 2491); Haggard (1925); Sayers *et al.* (1925 BM Bull. 231); Gerbis (1927); Schütze (1927); Flury (1928); Walton and Witherspoon (1928); Aves (1929); Yant (1930); Scheidemantel (1933); McCallan and Setterstrom (1940); Thornton and Setterstrom (1940); Weedon, Hartzell and Setterstrom (1940); Slater (1950); Ahlbrog (1951); Kaipainen (1954); Hurwitz and Taylor (1954); Breysse (1961); Milby (1962); Kleinfeld, Geil and Rosso (1964); Kemper (1966); C.L. Evans (1967); Prouza (1970); Simpson and Simpson (1971); Anon. (1975 LPB 3, p. 17); Thom and Douglas (1976); Archibald (1977); NIOSH (1977 Crit. Doc. 77–158); Vernot *et al.* (1977); NRC (1979); R.P. Smith and Gosselin (1979); WHO (1983 ECH 19); HSE (1985 LPB 63); Lynskey (1985 LPB 63); Amman (1986); Holton and Montague (1988); Kohout *et al.* (1988); R.M. Turner and Fairhurst (1990c)
Methyl isocyanate: Kimmerle and Eben (1964); ten Berge (1985)
Phosgene: Lehmann (1893); Muller (1910); Hess (1911); Dunn (1918); Meek and Eyster (1920); Underhill (1920); Winternitz *et al.* (1920); Flury (1921a, 1928); Laqueur and Magnus (1921); Zeehuisen (1922); Haggard (1924); Chlopin (1927–); Anon. (1928); Hegler (1928); Zangger (1932); Loschke (1933); Prentiss (1937); Kendall (1938); Sartori (1939); Cameron, Courtice and Foss (1941); Wachtel (1941); Waitt (1942); Boyland, McDonald and Rumens (1946); Courtice and Foss (1946); Weston and Karel (1946, 1947); Bickenbach (1947); Box and Cullumbine (1947); Karel and Weston (1947); Gilman *et al.* (1948); A.T. Jones (1952); Suess and Lerner (1956); Henschler and Laux (1960); Ardran (1964); Zielhuis (1970); Kawai (1973); NIOSH (1976 Crit. Doc. 76–137); de Rooij, van Eick and van de Meent (1981); Diller and Zante (1982); Diller (1985); Mulder *et al.* (1986); Mehlman (1987); Zwart (1987); MHAP (1993)
Sulphur dioxide, sulphuric acid: API (75–25); WHO (ECH 8); Ogata (1884); G.W. Jones, Capps and Katz (1918); Zeehuisen (1922); Haggard (1924); Kennon (1927); Flury (1928); Kehoe *et al.* (1932); Weedon, Hartzell and Setterstrom (1939, 1940); McCallan and Setterstrom (1940); Thornton and Setterstrom (1940); Amdur, Silverman and Drinker (1952); Amdur, Schulz and Drinker (1952); Logan (1953); C.A. Mills (1957); Amdur (1958); Leong, MacFarland and Sellers (1961); Anon. (1953); Zielhuis (1970); NIOSH (1977 Crit. Doc. 74–111); Amdur, Dubriel and Creasia (1978); Bitron and Aharonson (1978); Hilado and Cumming (1978); Alarie (1980); Silbaugh *et al.* (1981); Grint and Purdy (1990); R.M. Turner and Fairhurst (1992)
Ozone: Slater (1974); BOHS (1979 Monogr. 3); HSE (1983 EH 38)
Toxic fumes from burning materials, fire extinguishants: BRE (1974 CP 5/74, CP 11/74, CP 12/74); Underwood (1971); H.L. Kaplan and Hartzell (1984); Hartzell, Packham *et al.* (1985); Hartzell, Stacy *et al.* (1985); Hartzell, Priest and Switzer (1985); Alexeeff *et al.* (1986); Doe *et al.* (1986); Hartzell, Grand and Switzer (1987); Tsushiya and Nakaya (1986); Hartzell (1989); G.T. Atkinson, Jagger and Kirk (1992); Babrauskas *et al.* (1992); D.A. Carter (1992); Babrauskas (1993)

Ultratoxics (*see also* Table A3.1)
Lamanna (1959)

Table 18.2 *Selected references on toxic release*

Plant design and operation (*see also* Table 18.1)
Crocker (1970); AIChE (1972/65); HM Chief Alkali Inspector (1974); Chementator (1975, Apr. 14, 33; Jul. 7, 34; 1977, Jan. 3, 37); Kiang (1976); Archibald (1977); Mukerji (1977); Payne (1978); Buxton (1980); Hewitt (1980); D. Hughes (1980); G.A. Hunt (1980); IChemE (1980/120); Lamb (1980); A. Price (1980); Mecklenburgh (1982); Prugh (1985–); Zanetti (1986a,b); ILO (1989); Grigoriev, Polyakov and Artemev (1990); Sutherland (1990); N.C. Harris (1991); Kuryla (1993)

Toxic gas detectors (*see also* Table 18.1)
R. Zanetti (1986b); Atallah and Guzman (1987)

Toxic release mitigation
N.C. Harris (1987); Hiltz and Brugger (1989); Fthenakis and Zakkay (1990); Schatz and Koopman (1990); van Zele and Diener (1990); Diener (1991); Porter (1991)
Foam: Dimaio and Norman (1988, 1990); E.C. Norman and Swihart (1990)

Emergency planning
Duff and Husband (1974); Zajic and Himmelman (1978); Purdy and Davies (1985 LPB 62)

Shelter
D.J. Wilson (1987, 1990, 1991b); Glickman and Ujihara (1990); D.J. Wilson and Zelt (1990); Zelt and Wilson (1990); McQuaid (1991); Kakko (1992)

Protective clothing
Daugherty, Watson and Vo-Dinh (1992)

Decontamination
W.L. Owen, Sartor and van Horn (1960); Ayers (1964); P.E. James and Wilkin (1969); P.E. James and Menzel (1973); AEC (1975)

Hazard assessment
G.D. Bell (n.d.); Howerton (n.d., 1969); Simmons, Erdmann and Naft (1973, 1974); Dicken (1974, 1975); J.D. Reed (1974); van Ulden (1974); Westbrook (1974); Eisenberg, Lynch and Breeding (1975); Simmons and Erdmann (1975); Hewitt (1976); Sellers (1976); Solomon (1976); Solomon, Rubin and Okrent (1976); Lautkaski and Mankamo (1977); V.C. Marshall (1977d, 1982b); HSE (1978b); Zajic and Himmelman (1978); Napier (1979a); N.C. Harris (1982, 1985); Mecklenburgh (1982); Pantony and Smith (1982); Fiksel (1985); Pape and Nussey (1985); IChemE (1986/128); Pietersen (1986c); Withers and Lees (1986a); Baldini and Komosinsky (1988); Thomson and Nightingale (1988); Boykin and Levary (1989); J.K.W. Davies (1989a); Egol (1989a); Gephart and Moses (1989); Vergison, van Diest and Basler (1989); G.T. Atkinson, Jagger and Kirk (1991); Bützer and Naef (1991, 1992); Grint and Purdy (1990); Nussey, Mercer and Clay (1990); R.F. Griffiths (1991a,b); Touma and Stroupe (1991); Touma *et al.* (1991); Geeta, Tripathhi and Narasimhan (1993); Goldsmith and Schubach (1993); Dunbar *et al.* (1994); Tyler *et al.* (1994)

Particular chemicals
Acrylonitrile: Siccama (1973); Solomon, Rubin and Okrent (1976)
Ammonia: Resplandy (1967); W.L. Ball (1968b); Inkofer (1969); Medard (1970); Comeau (1972); MacArthur (1972); J.D. Reed (1974); Eisenberg, Lynch and Breeding (1975); Lonsdale (1975); Luddeke (1975); V.C. Marshall (1977b); HSE (1978b); Harvey (1979b); Baldock (1980); R.F. Griffiths (1981a); Raj (1982); R.H. Roberts and Handman (1986); Markham (1987b); Gephart and Moses (1989); Pallen (1990); Sutherland (1990); Langeluedecke (1991)
Chlorine: G.D. Bell (n.d.); Howerton (n.d., 1969); Hanslian (1937); Prentiss (1937); Romcke and Evensen (1940); Simmons, Erdmann and Naft (1973, 1974); Dicken (1974, 1975); Westbrook (1974); Eisenberg, Lynch and Breeding (1975); Chlorine Institute (1975 MIR-71, 1982 Pmphlt 74); Haber (1975, 1986); Sellers (1976); Solomon, Rubin and Okrent (1976); V.C. Marshall (1977b); HSE (1978b); Harvey (1979b); Meslin (1981); Emerson, Pitblado and Sharifi (1988); J.L. Woodward and Silvestro (1988); Anon. (1989 LPB 86, p. 1); Deaves (1989); Gephart and Moses (1989); Lin and Shroff (1991); Anon. (1993 LPB 113, p. 26)
Hydrogen cyanide: Solomon, Rubin and Okrent (1976)
Hydrogen fluoride: Crocker (1970); HSE (1978b); Hague and Pepe (1990); Schatz and Koopman (1990); Tilton and Farley (1990); van Zele and Diener (1990); Diener (1991)
Hydrogen sulphide: Echols (1976); Linskey (1985 LPB 63); Anon. (1989 LPB 87, p. 1); D.J. Wilson (1991a)
Phosgene: V.C. Marshall (1977b)
Sulphur dioxide: Sumner and Pfann (1976); Nyren and Winter (1987)
Vinyl chloride: McKinnon (1974); Kiang (1976); Mukerji (1977)

Indicators of cloud contour, including vegetation damage
Fryer and Kaiser (1979 SRD R152); Arner, Johnson and Skovronski (1986); R.F. Griffiths and Smith (1990)

Simulation of accidents
M.P. Singh, Kumar and Ghosh (1990)

ACGIH/16) and *Work Related Lung Disease Surveillance Report* (NIOSH, 1991/20).

18.1.1 Modes of exposure

Toxic chemicals enter the body in three ways: (1) inhalation, (2) ingestion, and (3) external contact. Generally, gases, vapours, fumes and dusts are inhaled and liquids and solids are ingested. Entry may also occur through the intact skin or the mucous linings of the eyes, mouth, throat and urinary tract.

18.1.2 Effects of exposure

Exposure to some chemicals results in temporary or permanent damage to organs of the body, i.e. poisoning. There is a wide variety of types of damage caused by toxic substances.

The effects of exposure to toxic chemicals may be acute or chronic. Acute effects result from a single exposure to a high concentration of the chemical; chronic effects result from exposure to low concentrations, perhaps over a large part of a working lifetime. With the latter type of exposure the effects may be latent and may show themselves only after many years. It is also possible for the effects of a single exposure to a high concentration to be latent.

A toxic chemical may induce a graded or a quantum response. A graded response refers to the symptoms shown by an individual, which become progressively more severe as the dose in increased. Exposure to carbon monoxide, for example, results in a set of symptoms of increasing severity. The graded responses for this and other gases are shown in Table 18.3.

A quantum response, on the other hand, refers to the effect of a toxic chemical on a population, in which some individuals suffer the defined injury and others do not. A person either has or does not have mesothelioma from crocidolite ('blue') asbestos. In this case it is the proportion of cases in the population which rises with an increasing dose level.

Table 18.3 *Effects of different concentrations of some toxic gases*

Gas	*Concentration*	*Reference*[a]
Ammonia	(ppm)	
TLV[c]	25	ACGIH
Concentration detectable by odour	20	Matheson
Concentration causing severe irritation of throat, nasal passages and upper nasal tract	400	Matheson
Concentration causing severe eye irritation	700	Matheson
Concentration causing coughing, bronchial spasms, possibly fatal for exposure of less than $\frac{1}{2}$ hr	1700	Matheson
Concentration causing oedema, strangulation, asphyxia, fatal almost immediately	5000	Matheson
Carbon monoxide	(% v/v)	
TLV	0.005 (50 ppm)	ACGIH
Concentration inhalable for 1 h without appreciable effect	0.04–0.05	Matheson
Concentration causing a just appreciable effect for exposure of 1 h	0.06–0.07	Matheson
Concentration causing unpleasant symptoms but not dangerous for exposure of 1 h	0.1–0.12	Matheson
Concentration dangerous for exposure of 1 h	0.15–0.2	Matheson
Concentration fatal for exposure of less than 1 h	0.4	Matheson
Chlorine	(ppm)	
TLV	1	ACGIH
Minimum concentration detectable by odour	1	*Chlorine Code*
	3.5	Matheson
Maximum concentration inhalable for 1 h without damage	4	Matheson
Minimum concentration causing throat irritation	15	Matheson
Minimum concentration causing coughing	30	Matheson
Concentration dangerous for exposure of $\frac{1}{2}$ h	40–60	Matheson
Concentration probably fatal after a few deep breaths	1000	Matheson
Hydrogen sulphide	(ppm)	
TLV	10	ACGIH
Concentration causing slight symptoms after exposure of several hours	70–150	Matheson
Maximum concentration inhalable for 1 h without serious effects	170–300	Matheson
Concentration dangerous for exposure of $\frac{1}{2}$–1 h	400–700	Matheson
Phosgene	(ppm)	
TLV	0.1	ACGIH
Minimum concentration detectable by odour	0.5–2	*Phosgene Code*
	5.6	Matheson
Maximum concentration for exposure of 15 min	1	*Phosgene Code*
Minimum concentration affecting throat	3.1	Matheson
Concentration probably fatal for exposure of $\frac{1}{2}$ h	5	Matheson
Concentration dangerous for exposure of $\frac{1}{2}$–1 h	25	Matheson
Concentration rapidly fatal for short[b] exposure	50	*Phosgene Code*
Concentration capable of causing lung injury in 2 min	167	Matheson

[a] ACGIH – Threshold Limit Values for 1976 (HSE, 1977 EH 15).
Matheson – *Matheson Gas Data Book* (Matheson Company, 1961).
Chlorine Code – Code of Practice for Chemicals with Major Hazards: Chlorine (BCISC, 1975/1).
Phosgene Code – Code of Practice for Chemicals with Major Hazards: Phosgene (CISHC, 1975/3).
[b] Presumably several minutes; this code defines 15 min as a prolonged exposure.
[c] TLV, threshold limit value.

The effects of acute exposure to toxic chemicals include:

(1) irritation –
  (a) respiratory,
  (b) skin,
  (c) eyes;
(2) narcosis;
(3) asphyxiation –
  (a) simple,
  (b) chemical;
(4) systemic damage.

Inhalation of some substances (e.g. chlorine) causes respiratory irritation. This irritation can serve as a warning. There are some chemicals, however, which

reach a toxic level before they cause appreciable irritation and thus give no warning.

Some substances (e.g. hydrocarbon vapours) have narcotic effects so that the person's responses are affected and he may become exposed to an accident. With certain chemicals (e.g. toluene diisocyanate) the effect is that the person becomes euphoric and oblivious of danger so that he is liable to perform hazardous acts.

Gases which act as simple asphyxiants (e.g. nitrogen and helium) merely displace oxygen in the atmosphere so that the concentration falls below that needed to maintain consciousness. But there are also chemical asphyxiants (e.g. carbon monoxide and hydrogen cyanide) which have a specific blocking action and prevent a sufficient supply of oxygen from reaching the tissues.

The effects of chronic exposure to toxic chemicals tend to be induction of injury or disease. One of the most important of these diseases is cancer. Some chemicals induce cancer. In addition to these carcinogens there also mutagens, which induce gene changes, and teratogens, which induce birth defects.

Some chemicals are much more liable than others to accumulate in the body over the long term. Such bioaccumulative chemicals are particularly harmful.

Different toxic chemicals affect different sites in the body. The effect of such chemicals depends on the target organ.

It will be apparent, therefore, that it is difficult to express the toxicity of different chemicals in terms of a common equivalent. Use is sometimes made of the term 'chlorine equivalent'. This is discussed in the *First Report* of the ACMH, which makes the following observations:

> Toxicity depends on a number of factors and no simple hard and fast rules can be laid down. The mode of action depends not only on the nature of the chemical but upon the dose received and the time scale of exposure. Strictly speaking the term 'chlorine equivalent' can be given relevance only in connection with slow, corrosive irritant chemicals having similar solubility in inhalation. Chemicals such as sulphur dioxide, ammonia, acrolein and nitrogen dioxide are all irritant yet have such different sites of action and variable effects as to make even an approximate calculation of a 'chlorine equivalent' difficult. The problem becomes even more difficult when one considers the potential toxicity of chemicals such as carbon monoxide which are not predominantly irritant. Mechanisms of toxicity are almost as varied as the classes of chemical which could be released.

18.2 Toxic Substances

Some factors relevant to toxic substances include:

(1) generation of the substance;
(2) toxic concentrations;
(3) effects of exposure;
(4) detectability by odour;
(5) precautions in handling;
(6) leak detection;
(7) first aid.

Most toxic substances which present a hazard in the chemical industry are chemicals that are deliberately produced, but some are generated as by-products by accident. Carbon monoxide and carbon dioxide are generated by combustion processes either in the process itself or in fires. Nitrogen oxides may be given off in welding. Ultratoxics may arise from side reactions.

The number of chemicals used in industry is very large and grows each year. Various figures have been quoted for the numbers of chemicals involved. According to Langley (1978) in the decade prior to 1978 approximately 4 million new chemicals had been identified, although at least 75% of these had been cited only once in the literature. Of more practical relevance is the estimate of the UK Chemical Information Centre (UKCIS), also quoted by Langley, that there are some 20 000–30 000 chemicals manufactured in quantities greater than 1 te per annum.

For the number of new chemicals coming into use each year in the UK at this level of output, Langley gives an estimate of some 300–400. For the USA the annual number of new chemicals has been estimated as about twice this value.

The problems posed by toxic chemicals have generally been perceived primarily in terms of noxious effects resulting from chronic exposure to chemicals that possess a degree of toxicity which has not been appreciated. More recently, there has been increased concern over the threat of large scale acute poisoning from the accidental release of toxic chemicals.

Early instances of the discovery of the noxious properties of substances include those of radium, phosphorus, lead, asbestos and naphthylamines. More recent examples include: polychlorinated biphenyls (PCBs), vinyl chloride and benzene. Even if the toxicity of a particular substance has been established, instances of exposure may still occur.

Some examples of the discovery of toxic effects or of instances of exposure to a substance with known toxic effects which have made impact in the UK have been given by Pittom (1978) and include:

1965 Bladder cancer from antioxidants (rubber industry)
1972 Lead poisoning (Avonmouth, Isle of Dogs)
1974 Angiosarcoma from vinyl chloride (polyvinyl chloride (PVC) plants)
1975 Asbestos related diseases (Hebden Bridge)
1976 TCDD (2,3,7,8–tetrachlorodibenzo-*p*-dioxin) (Seveso)

The dates refer to the years when publicity was at its height.

It is necessary, therefore, to take measures to ensure that the long-term, or chronic, toxic hazard is kept under good control. Of particular importance is the control of exposure to carcinogens. One of the principal means of control is the establishment of exposure limits, or hygiene standards. Over the years these limit values have tended to be reduced, and in some cases the reductions have been dramatic. For example, in the USA the limits for asbestos were reduced over the period 1938-83 as follows (Corn and Corn, 1984): 1938, 30 fibres/cm^3; 1970, 12 fibres/cm^3; 1971, 2 fibres/cm^3; and 1983, 0.5 fibres/cm^3.

There have also been occasional large releases of toxic chemicals of which the escape of methyl isocyanate at Bhopal in 1984 was much the worst. Good control of the

acute toxic hazard posed by a large release is equally important.

18.3 Toxicity Assessment

18.3.1 Toxicity data

Comprehensive accounts of occupational health risks involving toxic hazards are given in a number of texts, including the following: *Toxicity of Industrial Metals* (Browning, n.d.a), *Toxicity of Industrial Organic Chemicals* (Browning, n.d.b), *Industrial Hygiene and Toxicology* (Patty, 1948–), with its later edition *Patty's Industrial Hygiene and Toxicology* (Clayton and Clayton, 1991 ACGIH/73); *Dangerous Properties of Industrial Materials* (Sax 1957-), with its later edition–*Sax's Dangerous Properties of Industrial Materials* (Lewis, 1992 ACGIH/89); *Toxicity and Metabolism of Solvents* (Browning, 1965); *Toxicology of Drugs and Chemicals* (Deichmann and Gerarde, 1969); *Hazards in the Chemical Laboratory* (G.D. Muir, 1971–); *Registry of Toxic Effects of Chemical Substances 1981–82* (Tatken and Lewis, 1984); *Rapid Guide to Hazardous Chemicals in the Workplace* (Sax and Lewis, 1986), with its later edition (Lewis, 1990 ACGIH/49); *Toxicology: the Basic Science of Poisons* (Casarett and Doull, 1975), with its later edition (Amdur, Doull and Klaassen, 1991, ACGIH/54); *Chemical Hazards in the Workplace* (Scott, 1989 ACGIH/29); *Neurotoxicity Handbook* (Singer, 1990 ACGIH/46); *Chemical Hazards of the Workplace* (Hathaway *et al.*, 1991 ACGIH/55); *Hazardous Chemicals Desk Reference* (Lewis, 1991 ACGIH/60); and *Handbook of Toxic and Hazardous Chemicals and Carcinogens* (Sittig, 1991 ACGIH/59).

The American Conference of Government Industrial Hygienists (ACGIH) and the American Industrial Hygiene Association (AIHA) issue a number of publications on exposure limits for toxic chemicals. These are considered in Section 18.5.

The National Institute for Occupational Safety and Health (NIOSH) issues *Criteria Documents* for a large number of chemicals and also several other series: *Occupational Hazard Assessments*, *Joint Occupational Health Recommendations* and *Special Hazard Reviews*. Other publications include *Occupational Health Guidelines for Chemical Hazards* (NIOSH, 1981/6) and *Pocket Guide to Chemical Hazards* (NIOSH 1990/18). The OSHA also issues the *Chemical Information Manual* (OSHA, 1991/1).

Chemical Safety Data Sheets on toxic chemicals were formerly issued by the Manufacturing Chemists Association (MCA), but many of these have been withdrawn.

Information on toxicity is given in a number of publications by the Health and Safety Executive (HSE). EH 40/94 *Occupational Exposure Limits 1994* (HSE, 1994) is supported by EH/64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992). Series relevant to toxicity are the *Environmental Hygiene* (EH) series, the *Medical* (MS) series and the *Toxicity Review* (TR) series.

There are a number of databases for the toxicity of chemicals, many of which are available on computer. They include the following:

CHRIS	Chemical Hazard Response Information System (US Coast Guard)
OHMTADS	Oil and Hazardous Materials Technical Assistance Data System (Environmental Protection Agency (EPA))
RTECS	Registry of Toxic Effects of Chemical Substances (NIOSH)
TOXLINE	National Library of Medicine toxic substances database
HSELINE	HSE toxic substances database

An account of these and other systems is given in Chapter 29.

There is a good deal of guidance available on the handling of individual toxic substances. An early compilation was the *Gas Data Book* (Matheson Company, 1961). This deals with toxic concentrations, symptoms of exposure, precautions in handling and first aid.

Much relevant information is given in materials safety data sheets (MSDSs), which are described in Chapter 8. There are a number of MSDS compilations. They include *Compilation of Safety Data Sheets for Research and Industrial Chemicals* (Keith and Walters, 1985–), *Chemical Safety Data Sheets* (Walsh, 1988, vol.1; A. Allen, 1988, vols 2–5), *Chemical Safety Data Sheets* (Kluwer Publishers, 1992) and *Croner's Substances Hazardous to Health* (Kellard, 1993).

Other guidance is given in codes such as *Codes of Practice for Chemicals with Major Hazards* by the Chemical Industries Association (CIA) and in the EH series of the HSE.

The toxicity of chemicals is a field in which, at present, the situation changes particularly rapidly and the importance of seeking the most up-to-date information cannot be too strongly emphasized.

18.3.2 Toxicity testing

Information on toxicity is often incomplete or non-existent. This is not surprising, since the number of chemicals used in industry is so large. Therefore, in some cases it is necessary to conduct tests in order to obtain information on toxicity. Toxicity testing is now a well established activity which is conducted to ensure safety not only in the manufacture of chemicals but also in the use of food, drugs and cosmetics. General accounts are given by Hemsworth (1974), J.T. Carter (1976) and Neal and Gibson (1984).

Methods which are used to assess toxicity include (1) micro-organism tests and (2) animal experiments. The object of toxicity testing is to obtain quantitative information on toxic effects. The simple classification of substances as 'toxic' or 'non-toxic' is of little value.

Toxicity testing is expensive. According to C.R. Pearson (1982) the cost of the Base Set of tests required under the EEC Sixth Amendment to the Dangerous Substances Directive is £25 000–50 000. Detailed information on cost of specific tests for the USA is given by A.S. West (1986). He also estimates the costs of the EEC Premanufacturing Data Set of tests and of the Level 1 and Level 2 sets as $100 000, $500 000 and several million dollars, respectively.

The assessment of toxicity is a matter for experts. There are a number of organizations which specialize in toxicity testing and assessment, as described below.

18.3.3 Micro-organism tests

Accounts of micro-organism tests are given in *In Vitro Toxicity Testing of Environmental Agents* (Kolber *et al.* 1983) and by Neal and Gibson (1984). Studies of the effects of chemicals on micro-organisms are used for screening chemicals, particularly for possible carcinogenic, mutagenic or teratogenic effects. Developments in this area include, in particular, the tests used by Ames and co-workers (Ames, 1971).

18.3.4 Animal experiments

The other main type of test is experimentation on animals. This allows the use of the normal techniques of controlled experimentation. Although some earlier work made use of other animals such as monkeys, dogs, cats and rabbits, the animals now almost universally used are mice and rats.

The testing is done according to a strict protocol. The animal is given a fixed dose of chemical or is exposed to a gas of a given concentration for a fixed time and its health is then monitored for a defined observation period. Pathological investigation may also be performed. For certain types of test, such as those on inhalation toxicity, the observation period may be 10–14 days. For other types, such as those on carcinogens, it may extend to 2 or 3 years.

For many tests the objective is to determine the dose or concentration which is lethal to 50% of the animals. This is the lethal dose LD_{50} for an orally administered substance and the lethal concentration LC_{50} for an inhaled gas (see Section 18.11). In the latter case the period of exposure must also be defined. Frequently there is a legislative requirement for the determination of the LD_{50} as an index of toxicity. The corresponding index of aquatic toxicity is the median tolerance limit TL_mx, which is the concentration lethal to 50% of the test species for an exposure period of x hours.

There are various problems in the use of animal experiments. The first of these is the ethical problem. For this reason there are increasing pressures to limit such experiments to those for which high priority can be established.

Animal experiments are also both expensive and time-consuming. As already mentioned, experiments on the long-term effects of exposure to low concentrations of chemicals may involve extensive observation periods.

In order to obtain statistically valid results it is necessary to use quite large numbers of animals. This is a problem in almost all instances, but particularly so where the level of risk which is of interest is low. There is then the further problem of interpreting the results obtained and extrapolating them from other species to man.

18.3.5 Epidemiology

Another approach to the assessment of toxicity is epidemiology. Epidemiological studies are based on comparisons of disease or abnormality between the group under study and a control group. This approach is applicable to situations where a number of people have been exposed, often, though not always, over a period of years.

Accounts of epidemiology are given in *Medical Record Linkage* (Acheson, 1967), *Epidemiology and Disease* (J.P. Fox, Hall and Elvaback, 1970), *An Introduction to Epidemiology* (Alderson, 1976), *Guide for the Management, Analysis and Interpretation of Occupational Mortality Data* (NIOSH, 1990/19), *Exposure Assessment for Epidemiology and Hazard Control* (Rappaport and Smith, 1991 ACGIH/56), and by Harrington (1980a) and Neal and Gibson (1984).

There have been a number of important epidemiological investigations of toxic substances, including those of radium, β-naphthylamine, lead, asbestos and vinyl chloride.

Epidemiological studies have the great drawback that, by their nature, they yield information on the existence of a toxic effect only after people have fallen victim to it. This drawback is most serious where the effects are latent rather than acute, because in this case even the initiation of control measures cannot prevent disease, due to the backlog of previous exposure. This problem of lag has become much more important as the rate at which new substances are introduced has increased. Despite this, epidemiology is an important tool for toxicity assessment, as evidenced by the number of chemicals which have been identified as noxious by this means.

There are certain methodological problems in the epidemiological approach. One is the difficulty of determining the degree of exposure. In some cases, for example, the best estimate which investigators have been able to make of the level of exposure has been the threshold limit value current in the period concerned. Another difficulty is in defining the control group.

In practice, where a positive correlation is obtained between exposure and disease, this tends to be in cases in which a relatively small number of people have been exposed to quite high concentrations. Conversely, cases where a large number of people have been exposed to low concentrations tend to yield negative results.

The epidemiological approach has certain limitations. It is relatively easy to show a correlation between an agent and a disease, but it may only be possible to establish a causal relation by experiments which cannot normally be justified. Another is that, whereas a rare disease can be detected as a relative excess of the disease among small numbers of people, the demonstration of a common disease as a relative excess requires the investigation of a large population.

The epidemiological method may be modified by investigating not only overt manifestations of the disease but also pre-disease phenomena such as those revealed by urine tests or radiography.

18.3.6 Toxic load

The correlation of toxicity data requires the definition of the toxic load. This is the independent variable in terms of which toxic injury is expressed. Toxic load is thus a form of injury factor.

In the case of an orally administered dose, the toxic load L is simply the dose d:

$$L = d \qquad [18.3.1]$$

In the case of an inhaled gas the toxic load is, in general, some function of concentration c and the time t:

$$L = f(c, t) \qquad [18.3.2]$$

This function may simply be the product

$$L = ct \quad [18.3.3]$$

but it may alternatively be of the form

$$L = ct^m \quad [18.3.4]$$

For acute inhalation toxicity of irritant gases the value of m for animals tends to be less than unity and is often of the order of 0.5 (Doe and Milburn, 1983).

18.3.7 Toxic load–response relation

Given the form of the toxic load, a correlation may be sought between the toxic load and the proportion of the population suffering a defined degree of injury. This correlation is the toxic load–response relation. This term is preferred here to the more usual dose–response relation, since toxic load is a more general term than dose.

A distribution which is widely used to correlate data for toxic injury, as for injury of other kinds, is the log-normal distribution. Associated with the log-normal distribution is the probit equation.

A particular problem arises at low levels of toxic load, because the precise relationship between toxic load and the proportion affected is a critical issue in setting exposure limits. Figure 18.1 illustrates two possible relations. With the linear relation A there is no lower limit below which there is no noxious effect, whereas with the sigmoidal relation B, there may be said to be a 'threshold' below which the effect of the toxic load is negligible.

It is frequently difficult to distinguish between these two types of curve and to establish whether there is or is not a threshold. This is the case particularly where the numbers of workers involved are small and the conditions of exposure are variable.

There are relatively few toxic load–response relations established for toxic substances. Apart from those for tobacco, alcohol and certain drugs, Acheson and Gardner (1981) recognize for cancer only two such relations: one for chrysotile asbestos and one for ionizing radiation. The former is that given in the work of Liddell, McDonald and Thomas (1977) in a study of the effect of chrysotile asbestos dust on some 11 000 workers in Quebec, which gives a linear relation passing close to the origin and is interpreted by these authors as indicating no safe threshold.

Further discussions of the toxic-load response are given by C.C. Brown (1984) and Snyder (1984). The latter describes different ways of plotting the load–response curve and gives a number of such curves obtained in animal experiments.

Various equations have been developed for the toxic load–response relations at low levels of toxic load, and statistical methods have been applied to obtain fits to the data. There are deficiencies, however, in a purely statistical approach and it may be more fruitful to support such work with exploration of the toxicokinetics. An example of work on these lines is that of Gehring, Watanabe and Park (1979), who studied the load–response relation for vinyl chloride by modelling the metabolism of the chemical in the body and examining different empirical equations for this relation in the light of the model. A further treatment of the relation between load–response curve and toxicokinetic modelling is given by C.C. Brown (1984).

18.3.8 Toxicokinetic modelling

The unsteady-state modelling of the effects of chemicals in the body is widely practised by pharmacologists, who have developed a number of pharmacokinetic models. The typical model is for a drug which is taken in a single dose. Accounts of such models include those given for E. Nelson (1961), Casarett and Doull (1975), Tuey (1980), Rogers, Spector and Trounce (1981) and Albert (1985).

One of the simplest models is the one-compartment model with finite rate elimination, which is illustrated in Figure 18.2. For this model the two cases commonly treated are the impulse and the step response, the first corresponding to the instantaneous introduction of the chemical and the second to the constant input of the chemical into the body, the prior concentration being zero in both cases. For the first case

$$\frac{dX}{dt} = -k_e X \quad [18.3.5]$$

with

$$X(0) = D_0 \quad [18.3.6]$$

where D_0 is the dose of the chemical, k_e is the elimination constant and X is the mass of chemical in the body. For the second case

$$\frac{dX}{dt} = D - k_e X \quad [18.3.7]$$

where D is the dose rate. The concentration C is given by

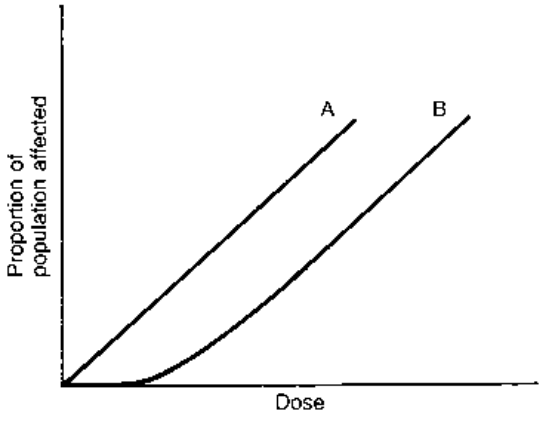

Figure 18.1 *Some idealized load–response relations for quantum response*

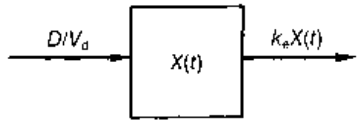

Figure 18.2 *One compartment model of a toxic chemical in the human body*

$$C = X/V_d \quad [18.3.8]$$

where V_d is the apparent volume of distribution of the chemical in the body. The chemical is distributed between the bloodstream and other body matter, both aqueous and non-aqueous, and the total effective capacity constitutes the apparent volume of distribution. For elimination after an instantaneous input of the chemical

$$C = C(0)\ \exp(-k_e t) \quad [18.3.9]$$

From Equation 18.3.5 the half-life $t_{\frac{1}{2}}$ of the chemical in the body is $0.693/k_e$. Some typical half-lives of drugs in the body, as given by Albert (1985), are aspirin 0.3 h, morphine 3 h, quinidine 6 h, diazepam 50 h and phenobarbital 86 h.

The model describes the variation of concentration with time of the chemical in the body and is based on the assumption that the body has a mechanism for elimination of the chemical. Elimination occurs by metabolism or secretion.

Similar models may be used to explore toxic effects, and are then termed toxicokinetic models. Toxicokinetic models provide valuable guidance on the interpretation of empirical results, both in applying the results of animal experiments to man and in assessing the shape of the toxic load–response curve at low toxic loads.

18.3.9 Statistical interpretation

Statistical methods have an important part to play in the design and interpretation of animal experiments, in the interpretation of toxic load–response data and in estimating the parameters of correlations.

Accounts of the application of statistics to these problems are given in *The Statistics of Bioassay* (Bliss, 1952) and *Probit Analysis* (Finney, 1971).

For obvious reasons the number of animals which can be used in gas toxicity experiments has to be kept as low as possible and the statistical interpretation of the results is therefore crucial. It has been shown by Trevan (1927) that for a particular dose–mortality determination the confidence level depends on the number of animals and on the mortality. He applied the binomial expansion

$$(p+q)^N = 1 \quad [18.3.10]$$

where p and q are the probabilities of death and survival, respectively, and N is the number of animals in the experiment. Then for the distribution

Mean $= N\mathrm{p}$
Standard deviation $\sigma = (pqN)^{\frac{1}{2}}$
Confidence limits $= N\mathrm{p} + z\sigma$

where z is the number of standard deviations corresponding to the confidence level.

Applying Trevan's method with a 95% confidence level, the results given in Table 18.4 and Figure 18.3 are obtained. It can be seen that for experiments with small numbers of animals the confidence limits for 50% mortality are wide and those for other mortalities such as 25% (or 75%) and 10% (or 90%) they are even wider.

Thus for a given confidence level it is necessary to use more animals to determine an LC_{10} or LC_{90} than an LC_{50} (see section 18.11). Alternatively, and this is the more usual case experimentally, for a given number of animals the confidence in the LC_{10} and LC_{90} values is less than that in the LC_{50}.

Table 18.4 *Expected numbers of deaths in experimental animals (Withers and Lees, 1985a; after Trevan, 1927) (Courtesy of Elsevier Science Publishers)*

Mortality	*N*	*σ*	*zσ*	Np	*Range*
50%	10	1.581	3.099	5	2–8
	20	2.236	4.383	10	6–14
	30	2.739	5.368	15	10–20
	40	3.162	6.198	20	14–26
	50	3.536	6.931	25	18–32
	60	3.873	7.591	30	22–38
	70	4.183	8.199	35	27–43
	80	4.472	8.765	40	31–49
	100	5.000	9.800	50	40–60
25%	30	2.372	4.649	7.5	3–12
	100	4.330	8.487	25	17–33
10%	30	1.643	3.220	3	0–6
	100	3.000	5.880	10	4–16

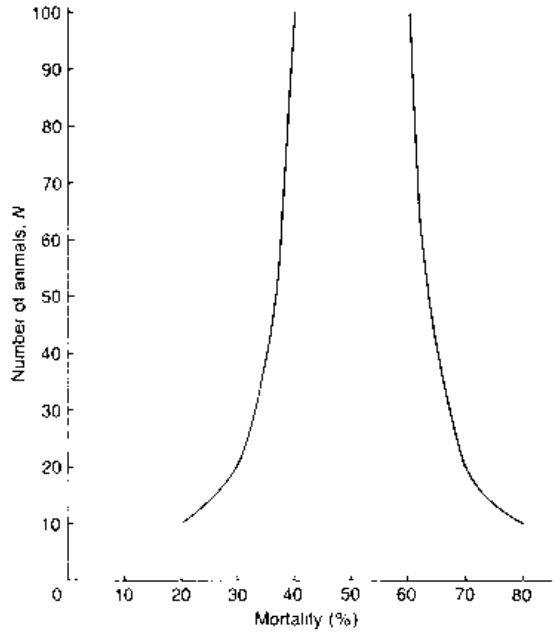

Figure 18.3 *Expected numbers of deaths in experimental animals (Withers and Lees, 1985a; after Trevan, 1927) (Courtesy of Elsevier Science Publishers)*

A method widely used for determining the lethal toxicity parameters and confidence limits in a study where groups of animals are exposed to different concentrations for a fixed period is that of Litchfield and Wilcoxson (1949). The method requires information on the numbers of animals and the numbers of

concentrations and yields the LC_{50}, the LC_{16} and the LC_{84} and the confidence limits.

18.3.10 Extrapolation between species

The application to man of results from experiments on animals is an area of considerable difficulty and uncertainty. With many substances different species exhibit similar reactions and extrapolation to man may be made. But there are also many examples of different reactions to the same chemical in different species. For example, penicillin causes lethal haemorrhage enteritis in guinea-pigs, but is used medically in man, while β-napthylamine, which is carcinogenic to man, does not cause bladder cancer in rats.

Accounts of the principles underlying the extrapolation of empirical results between species are given in *Detoxification Mechanisms* (R.T. Williams, 1959), *Hawk's Physiological Chemistry* (Oser, 1965), *Mammalian Protein Metabolism* (Munro, 1969) and *Drug Metabolism: From Microbe to Man* (Parke and Smith, 1977) and by Freireich *et al.* (1966), S.B. Baker, Tripod and Jacob (1970), Rall (1970), F.J. Miller, Menzel and Coffin (1978), Paddle (1980), Purchase (1980), Oser (1981), Menzel and Smolko (1984) and ten Berge and Zwart (1989).

One general principle is that the toxic effect is likely to be similar only if the target organ is the same in the two species. Another general principle is that what matters is the quantity of the toxin which reaches the target organ, rather than simply the quantity which enters the body. These two principles are applicable in the interpretation of the chronic effects of chemicals such as carcinogens.

The extent to which extrapolation can be made between two species is illustrated by the data given by Purchase (1980). He examined data on 250 chemicals tested for carcinogenicity on rats and mice and found the following results:

126 chemicals positive for cancer in rats; 87% positive for mice also
119 chemicals negative for cancer in rats; 82% negative for mice also
130 chemicals positive for cancer in mice; 84% positive for rats also
115 chemicals negative for cancer in mice: 85% negative for rats also

A widely used rule-of-thumb in toxicology is that if consistent results are obtained for three animal species, they may be treated, with caution, as applicable to humans.

For the inhalation toxicity of irritant gases, the target organ is the respiratory system and the quantity of toxic gas reaching the organ is relatively well defined. In this case the specific loads of toxic gas on the respiratory system of each species may be compared.

18.3.11 Toxic risk assessment

The information obtained from toxicity assessments of the kind just described may be used to make a toxic risk assessment for a particular chemical or plant. There are two rather different kinds of toxic risk assessment. One is the risk assessment undertaken by the regulatory agency in order to determine the precautions to be taken and to set the hygiene limits. The other is that carried

Table 18.5 *Some organizations involved in assessment of toxic hazards*

A EEC	
	Reference[a]
Advisory Committee on Safety, Hygiene and Health at Work (to Council of Ministers)	201
Association of Plastics Manufacturers in Europe	208
European Federation of Chemical Engineering (CEFIC) Committees	205
CONCAWE	208
European Industry Ecology and Toxicology Centre (ECETOC)	206

B UK	
	Reference[a]
Health and Safety Executive (HSE)	
Advisory Committee on Toxic Substances	
British Industrial Biological Research Association (BIBRA)	208
Chemical Industries Association	
Huntingdon Research Centre	
Medical Research Council (MRC), Toxicology Unit	

C USA	
	Reference[a]
Consumer Products Safety Commission (CPSC)	226
Department of Agriculture	238
Department of Health and Human Services	88
Environmental Protection Agency (EPA)	26
Food and Drug Administration (FDA)	218
National Institute for Occupational Safety and Health (NIOSH)	87
Occupational Safety and Health Administration (OSHA)	25
American Conference of Government Industrial Hygienists (ACGIH)	107
American Industrial Health Council	131
American Industrial Hygiene Association (AIHA)	102
Chemical Industry Institute of Toxicology (CIIT)	130
Chemical Manufacturers Association (CMA)	
Interagency Regulatory Liaison Group (IRLG)	238
Interagency Testing Committee (ITC)	A.S. West (1986)
National Academy of Sciences (NAS)	92
National Cancer Institute	86
National Center for Health Statistics	88
National Center of Toxilogical Research (NCTR)	82
National Institute for Environmental Health Sciences	239
Office of Science and Technology Policy (OSTP)	93
Office of Technology Assessment (OTA)	93

Society of Toxicology (SOT)	219
Programs	
Health Interview Survey (HIS)	88
Health and Nutrition Examination Survey (HANES)	88
National Cancer Program	70
National Toxicology Program (NTP)	78
Surveillance, Epidemiology and End Results Program (SEER)	87

[a] References are to page numbers in Deisler (1984b), unless otherwise stated.

out by a manufacturer in order to define the requirements for plant design and operation.

Accounts of toxic risk assessment are given in *Risk Assessment in the Federal Government: Managing the Process* (NAS/NRC, 1983), *Assessment and Management of Chemical Risks* (Rodricks and Tardiff, 1984a), *Toxicological Risk Assessment* (Clayson, Krewski and Munro, 1985), *The Risk Assessment of Environmental Hazards* (Paustenbach, 1989 ACGIH/37) and by Bridges (1985).

The National Academy of Sciences (NAS) report considers toxic risk assessment as involving four stages: (1) hazard identification, (2) dose–response assessment, (3) exposure assessment and (4) risk characterization.

Some of the problems of dose–response, or toxic load–response, assessment have already been considered. Clearly the existence or otherwise of a threshold value below which any noxious effect is negligible is a key issue. The definition of the level of exposure to be expected is also difficult but important. Once the risks have been assessed, they may be evaluated using suitable risk criteria.

In the USA, toxic risk assessment has been used in the setting of hygiene standards. Thus for inorganic arsenic, the Occupational Safety and Health Administration (OSHA) estimated, using a linear dose–response model, that for 1000 workers over a working lifetime there would be 8 excess deaths at a level of 10 mg/m^3, 40 at 50 mg/m^3 and 400 at 500 mg/m^3, and on the basis of this assessment reduced the hygiene standard from 500 to 10 mg/m^3. In justifying this decision, the OSHA stated

> The level of risk from working a lifetime of exposure at 10 mg/m^3 is estimated at approximately 8 excess lung cancer deaths per 1000 employees. OSHA believes that this level of risk does not appear to be insignificant. It is below risk levels in high risk occupations but it is above risk levels in occupations with average levels of risk.

18.3.12 Relevant organizations

There are a rather large number of organizations involved in the assessment of toxic hazards, as regulatory bodies, research institutes, industrial groupings and so on. Some of these are listed in Table 18.5. Brief accounts of the function and activities of many of these organizations are given by Deisler (1984b), as shown in the table.

18.4 Control of Toxic Hazard: Regulatory Controls

There is a world-wide trend towards much stricter regulatory control of toxic chemicals. Elements of such control include determination of the properties of the substances, limitation of emissions to the atmosphere, setting of limits for airborne concentrations, monitoring and control of airborne concentrations, monitoring of health of workers and assessment of risk to workers. The legislation in the EC, the UK and the USA on toxic chemicals has been outlined in Chapter 3. This section gives further details.

18.4.1 Control strategies

The control of the chronic toxic hazard needs to be based on a coherent strategy. The outline of such a strategy is given by Lowrance (1984), in a review which is concerned specifically with carcinogens, but which is of wider applicability. He argues that there is need for a framework which allows different risks to be compared and that the approach taken should be more explicit.

18.4.2 Regulatory controls in Europe

In the EC, the Sixth Amendment to the Dangerous Substances Directive (79/831/EEC) creates requirements for the notification and testing of new chemicals. Existing chemicals are listed in the European Core Inventory of Existing Substances (ECOIN) and the European Inventory of Commercial Chemical Substances (EINECS).

For new chemicals a manufacturer is required to submit a premarketing notification (PMN). The information required covers the chemical and its chemical and physical properties, the health effects, the ecological effects, the production volume and major uses, and the storage, transport and ultimate disposal. The level of manufacture which attracts notification is 1 te per annum. Intermediates for use only on site and polymers are excluded from the notification requirements. The inventory of chemicals is a static one. A manufacturer of a chemical must notify a new chemical which is not on the list, even if this has already been done by another manufacturer.

The information required on the properties of the chemical was originally defined in the Base Set given in the Sixth Amendment and subsequently specified in the minimum premarketing data (MPD) set shown in Table 18.6.

For chemicals to be manufactured in quantities larger than 1 te per annum further tests are required. The trigger levels are:

Marketing level (te/year)	*Tests required*
1–10	MPD set
10–100	Some Level 1 testing may be required
100 (or 500 te total)	Level 1
1000 (or 5000 te total)	Level 2

The Level 1 and Level 2 sets comprise further toxicology and ecotoxicology tests.

Table 18.6 *EC Minimum Premarketing Data set*

Physical/chemical data	
Melting point	Octanol/water partition coefficient
Boiling point	Flashpoint
Density	Flammability limits
Vapour pressure	Explosive properties
Surface tension	Auto-flammability
Water solubility	Oxidizing properties
Fat solubility	UV and visible spectra
Toxicity data	
Acute oral toxicity	Eye irritation
Acute dermal toxicity	Repeated dose (28 day)
Acute inhalation toxicity	Mutagenicity (bacterial)
Skin irritation	Mutagenicity (non-bacterial)
Skin sensitization	
Ecotoxicity data	
Fish acute toxicity	Degradation (biotic and abiotic)
Daphnia toxicity	

Accounts of the Sixth Amendment have been given by Langley (1978), C.R. Pearson (1982) and A.S. West (1986). An account by Rijkels (1984) on the control of carcinogens in Europe gives additional background. Further directives cover exposure to toxic chemicals (89/677/EEC) and carcinogens (90/394/EEC).

18.4.3 Regulatory controls in the UK

In the UK, the control of toxic substances has been primarily through the Health and Safety at Work etc. Act 1974 (HSWA) with the HSE as the enforcing authority. In particular, these arrangements have applied to control of toxic substances in the workplace and to hygiene standards.

The EC Sixth Amendment is implemented by the Notification of New Substances Regulations 1982. The requirements are essentially as described in the previous section. An account of the background to these regulations has been given by C.R. Pearson (1982).

The Control of Substances Hazardous to Health Regulations 1988 (COSHH) creates a comprehensive system of controls. HSE guidance is given in an associated ACOP L5 *Control of Substances Hazardous to Health and Control of Carcinogenic Substances* (HSE, 1988). The occupational exposure limits are given in EH 40/94 *Occupational Exposure Limits 1994* (HSE, 1994). The COSHH Regulations cover carcinogens and dusts. HSE guidance on carcinogens is given in the ACOP L5, as just described.

There are also regulations dealing with certain specific substances. They include the Lead at Work Regulations 1980 and the Control of Asbestos Regulations (CAWR) 1987. These are described below. More detailed accounts of the COSHH Regulations and the CAWR are given in Chapter 25.

The control of plants with major inventories of toxic chemical is exercised under the Control of Major Accident Hazards Regulations 1984 (CIMAH), as described in Chapters 3 and 4.

Requirements for the reporting of toxic releases are given in the Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1985 (RIDDOR), as described in Chapter 3.

18.4.4 Regulatory controls in the USA

In the USA, the OSHA has responsibility for the control of toxic substances in the workplace. It promulgates and enforces hygiene standards under the Occupatioal Safety and Health Act 1970. The OSHA may adopt by administrative action any health and safety standards in federal legislation or in codes or guidelines produced by consensus groups. It has in fact adopted various American National Standards Institute (ANSI) standards and many ACGIH threshold limit values.

The OHSA issues Permanent Health Standards. The list of standards, as of 1983, is shown in Table 18.7.

The Toxic Substances Control Act (TSCA) 1976 provides a framework for the control of toxic chemicals in manufacture and transport. The enforcing authority is the EPA, which has extensive duties and powers under the act. The TSCA has been described in a series of papers by A.S. West (1979, 1982, 1986).

The TSCA lays down requirements for the notification of new chemicals, and is in this respect the equivalent of the EC Sixth Amendment, but it also contains requirements for existing chemicals. Some principal sections of the TSCA are listed in Table 18.8. Existing chemicals are listed in the TSCA Chemical Substance Inventory (EPA, Office of Toxic Substances, 1979, 1982).

For new chemicals a manufacturer is required under Section 5 to submit a premanufacture notice (PMN). The information required covers the chemical, the health effects, the exposure of workers, the major uses and production volumes, the by-products and the ultimate disposal of the main product and by-products. There is no requirement for a base set of toxicity data, but an assessment is required of the health risk.

Table 18.7 *OSHA Permanent Health Standards 1983*[a]

Acrylonitrile	Coke-oven emissions
Arsenic	Cotton dust
Asbestos	1,2-Dibromo-3-chloropropane
Benzene	Lead
14 Carcinogens	Vinyl chloride

[a] Standards promulgated in accordance with the Occupational Safety and Health Act, Section 6(b).

Table 18.8 *Some principal sections of the Toxic Substances Control Act 1976*

Section	
4	Issue of testing rules for selected substances
	4(e) Establishment of priority list of chemicals
5	Premanufacture notices
6	Regulation of selected substances
7	Regulation of imminent hazards
8	Reporting and retention of information
	8(a) Reporting on existing chemical substances
	8(e) Notice of substantial risks

Table 18.9 *Factors to be considered by EPA under the Toxic Substances Control Act 1976 in regulating and in establishing a rule for testing a chemical*

A Regulation of a chemical
1 Effects on health and magnitude of exposure of human beings
2 Effects on the environment and magnitude of exposure of the environment
3 Benefits of various uses and the availability of substitutes for each use
4 Reasonably ascertainable economic consequences of regulation after consideration of the effect on the national economy, small business, technological innovation, the environment and public health
B Rule for testing a chemical
1 The relative costs of the various test protocols and methodologies
2 The reasonably foreseeable availability of facilities and personnel to perform such tests
Health and environmental effects for which standards for development for test data may be prescribed include:
1 Carcinogenesis
2 Mutagenesis
3 Teratogenesis
4 Behaviour disorders
5 Cumulative or synergistic effects
6 Any other effect related to unreasonable risk of injury to health or the environment
Characteristics for which standards may be prescribed include:
1 Persistence
2 Acute toxicity
3 Subacute toxicity
4 Chronic toxicity
5 Any other characteristic which may present such a risk

Notification is attracted at any level of manufacture. Intermediates used only on site are included, as are polymers, with some exceptions, but chemicals in research and development are excluded. Once a chemical has been notified by a single manufacturer, it is added to the TSCA Inventory, which is therefore a dynamic inventory.

While the TSCA is broadly similar to the Sixth Amendment, there are some important differences. The TSCA covers existing as well as new chemicals and it has no threshold level for notification, but there is no requirement for a base set of toxicity data and the inventory of chemicals is dynamic. Detailed comparisons are given by Doyal and Epstein (1983) and A.S. West (1986).

Under Section 4 of the TSCA, the EPA is both empowered and required to initiate toxicity testing of existing chemicals. Recommendations for such testing are made by the Interagency Testing Committee (ITC), which issues periodic lists. The EPA is required to initiate testing or show cause why it has not done so, and it also issues periodic lists of chemicals for priority testing.

The factors which the EPA is required to take into account in regulating a chemical and in establishing a rule for testing a chemical are specified in Section 6 of the TSCA, and are listed in Table 18.9, Sections A and B, respectively.

There have been a number of important legal cases which influence the control of toxic chemicals in the USA. The Delaney Amendment to the Federal Food, Drug and Cosmetic Act in 1958 banned the deliberate addition to food of any additive which is carcinogenic as determined from animal experiments or human response. This absolute requirement was subsequently modified on appeal to the effect that the Food and Drug Administration (FDA) was not required to bar containers in which very small amounts of a carcinogen, actually acrylonitrile monomer, were liable to migrate into the food.

In 1977, the OSHA promulgated an Emergency Temporary Standard for benzene, followed by a permanent rule, after an epidemiological study which seemed to show that benzene was more toxic than previously supposed. In the Benzene Case (Industrial Union Department vs American Petroleum Institute) in 1980, the Supreme Court set aside the benzene standard and ruled that the OSHA could not adopt a standard unless it finds both that there is a significant risk and that the standard will significantly reduce that risk.

The Formaldehyde Case (Gulf South Insulation vs United States Consumer Product Safety Commission) in 1983 involved a ban by the Consumer Product Safety Commission (CPSC) on urea formaldehyde foam insulation in homes and schools. The case centred on the interpretation of epidemiological data. The court took the view that the methodology and data used in extrapolating to low exposure levels were unsatisfactory and did not meet the substantial evidence criterion.

The control of major chemical hazards is exercised through Title III of the Superfund Amendments and Reauthorization Act (SARA) 1988, enforced by the EPA, as described in Chapters 3 and 4. SARA Title III, Section 6, requires the EPA to create a toxic chemicals inventory, the toxic release inventory (TRI).

These and other developments in the control of toxic chemicals in the USA may be followed through the references given in Table A1.4.

18.5 Hygiene Standards

There are two main types of toxic limit. For exposure over a working lifetime there are hygiene standards in the form of occupational exposure limits, whilst for emergency exposure there are emergency exposure limits. Occupational hygiene standards are considered in this section and in Section 18.7, and emergency exposure limits are considered in Section 18.10.

Three principal sets of occupational hygiene standards are the threshold limit values used in the USA, the occupational exposure limits used in the UK and the MAK-Werte used in Germany.

18.5.1 US Threshold limit value system

A set of threshold limit values (TLVs) is published in the USA by the American Conference of Government Industrial Hygienists (ACGIH). The TLV system is widely used, not only in the USA but also in many other countries.

The US TLVs are given in the *Threshold Limit Values and Biological Exposure Indices 1992-1993* (ACGIH, 1992/80). Other related documents are the *Guide to Occupational Exposure Values - 1992* (ACGIH, 1992/78), which also gives the German MAK-Werte; *Documentation of Threshold Limit Values and Biological Exposure Indices* (ACGIH/3); and *Documentation for the Biological Exposure Indices* (ACGIH/1).

There are a number of critiques of the TLV system, including that by Doyal and Epstein (1983).

18.5.2 Former UK threshold limit value system

As far as concerns the limits for workplace exposure to toxic chemicals in the UK, for many years use was made of a modified version of the US TLV system. This replaced an earlier system based on maximum allowable concentrations (MACs). In 1980 the UK moved to a system of occupational exposure limits (OELs). The latter system is described in the following section.

Since the TLV system has now been superseded, it is not appropriate to give a detailed description here. On the other hand, the TLV system is referred to frequently in the literature and is still in widespread use in many countries. The general nature of the system is indicated by the following information taken from EH 15 *Threshold Limit Values for 1976* (HSE, 1977).

In order to avoid misuse, the nature and limitations of TLVs need be appreciated. Some principal features are:

(1) a TLV is not a sharp dividing line between 'safe' and hazardous concentrations;
(2) the absence of a substance from the list does not mean that it is necessarily safe;
(3) the best practice is to keep the concentration of a substance in the atmosphere to a minimum, regardless of whether it is known to present a hazard and whatever the value of the TLV;
(4) the application of a TLV to a particular case is a specialist matter.

There are three categories of TLV: (1) threshold limit value, time-weighted average (TLV-TWA); (2) threshold limit value short-term exposure limit (TLV-STEL); and (3) threshold limit value–ceiling (TLV-C).

The TLV-TWA is the time-weighted average concentration for a normal 8-hour workday or 40-hour workweek to which nearly all workers may be repeatedly exposed, day after day, without adverse effect. Excursions above the limit are allowed, provided they are compensated by other excursions below the limit. There is also a limit on the maximum concentration. In some cases it may be permissible to use the average concentration over a workweek rather than over a workday.

The TLV-STEL is the maximum concentration to which workers can be exposed for a period of 15 minutes continuously without suffering from (1) intolerable irritation, (2) chronic or irreversible tissue change, or (3) narcosis of sufficient degree to increase accident proneness, impair self-rescue or materially reduce work efficiency, provided that no more than four excursions per day are permitted, with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA is not exceeded.

The TLV-C is the concentration which should not be exceeded even instantaneously. Substances which are given a TLV-C are those which are predominantly fast-acting and require a limit related to this aspect.

The TLVs on the list are expressed in two units: ppm (parts of gas or vapour per million parts of contaminated air at 25°C and 760 mm Hg) and mg/m^3 (milligrams of substance per cubic metre of air). For particulate materials the unit is mppcf (millions of particles per cubic foot of air).

TLVs are based on the best available information from industrial experience and from experimental studies of humans and animals and, where possible, from all three. The basis of the values thus varies. In some cases it is freedom from irritation, narcosis or other stress, in others it is the absence of effects impairing health.

The limits based on physical irritation should be regarded as equally binding as those based on health impairment, since there is increasing evidence that irritation can initiate or promote impairment.

There is a wide variation in the susceptibility of individuals to low levels of airborne contaminants. A small proportion may be seriously affected.

The nature and amount of information on which a TLV is based varies widely and the degree of confidence which can be placed in a particular TLV is therefore variable.

TLVs are intended for use in industrial hygiene and their interpretation is a specialist matter. They should not be used or adapted for other purposes, in particular not (1) as a relative index of toxicity, (2) for air pollution work, or (3) for the assessment of toxic hazard from a continuous, uninterrupted exposure. They should also not be used as proof or disproof of an existing disease or physical condition or in countries where working conditions differ substantially from those in the USA.

The use of a TLV implies that there must be a system for monitoring the concentration of the substance in the air and that the measurements must be, if not continuous, at least frequent enough for the purpose.

In addition to giving TLVs, EH15 also deals with the following:

(1) skin effects;
(2) mineral dusts;
(3) nuisance particulates;
(4) simple asphyxiants;
(5) carcinogens.

18.5.3 Other OSHA limits

There are a number of other limit values. Some which are used by the OSHA include:

STEL — Short term exposure limit: maximum exposure concentration for a period of exposure less than a workshift

MAC — Maximum acceptable ceiling: maximum exposure concentration regardless of period of exposure

Table 18.10 *Occupational exposure limits (OELs) of some chemicals (HSE, 1994 EH 40) (Courtesy of HM Stationery Office)*

A Maximum exposure limits (MELs)

	Long-term exposure limit (8-hour TWA reference period)		*Short-term exposure limit (15-minute reference period)*		*Note*
	(ppm)	(mg/m^3)	(ppm)	(mg/m^3)	
Acrylonitrile	2	4			Sk[a]
Asbestos	See EH 40				
Benzene	5	16			
Buta-1,3-diene	10	22			
Carbon disulphide	10	30			Sk
Ethylene oxide	5	10			
Formaldehyde	2	2.5	2	2.5	
Hydrogen cyanide			10	10	Sk
Isocyanates, all (as NCO)		0.02		0.07	Sen[b]
Lead compounds	See EH 40				
Silica		0.4			
Styrene	100	420	250	1050	
Trichloroethylene	100	535	150	802	Sk
Vinyl chloride[c]	7				

B Occupational exposure standards (OESs)

	Long-term exposure limit (8-hour TWA reference period)		*Short-term exposure limit (15-minute reference period)*		*Note*
	(ppm)	(mg/m^3)	(ppm)	(mg/m^3)	
Acetone	750	1780	1500	3560	
Ammonia	25	17	35	24	
Carbon dioxide	5000	9000	15000	27000	
Carbon monoxide	50	55	300	330	
Carbon tetrachloride	See EH 40				
Chlorine	0.5	1.5	1	3	
Ethylene glycol, vapour[d]		60		125	
Hydrogen chloride			5	7	
Hydrogen fluoride (as F)			3	2.5	
Hydrogen sulphide	10	14	15	21	
Isopropanol[e]	400	980	500	1225	Sk
LPG[f]	1000	1800	1250	2250	
Methanol	200	260	250	310	Sk
Naphthalene	10	50	15	75	
Nitric acid	2	5	4	10	
Nitrobenzene	1	5	2	10	Sk
Nitrogen dioxide	3	5	5	9	
Nitrogen monoxide	25	30	35	45	
Ozone	0.1	0.2	0.3	0.6	
Phenol	5	19	10	38	
Phosgene[g]	0.1	0.4			
Sulphur dioxide	2	5	5	13	
Toluene	50	188	150	560	Sk

[a] Sk, can be absorbed through the skin
[b] Sen, capable of causing respiratory sensitization. The identified substances are those which: (1) are assigned the risk phrase R42: 'may cause sensitization by inhalation' in Part IA1 of the Approved List; (2) are listed under the Social Security Act 1975 or Schedule 2 of the Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1985 in connection with prescribed or reportable diseases, respectively.
[c] Vinyl chloride is also subject to an overriding MEL of 3 ppm, as described in EH 40.
[d] Ethane-1,2-diol.
[e] Propan-2-ol.
[f] Liquefied petroleum gas.
[g] Proposed change for 1995 is a long-term OES of 0.02 ppm (0.08 mg/m^3) and a short-term OES of 0.06 ppm (0.25 mg/m^3).

PEL Permissible exposure limit: applied variously to the TLV, STEL or MAC
AL Action level: one-half the PEL; the concentration below which additional measurements of the same exposure will probably not exceed the PEL

18.5.4 MAKWerte limit system

The German system of hygiene standards is the MAK-Werte system. As stated above, values of the MAK-Werte are included in *Guide to Occupational Exposure Values – 1992* (ACGIH, 1992/78). The MAK-Werte and also the Technische Richtskonzentrazionen (TRK) systems are described by Rijkels (1984).

18.5.5 International exposure limits

An international set of occupational exposure limits are the *Occupational Exposure Limits for Airborne Toxic Substances,* published by the International Labour office (ILO, 1991/2).

As already mentioned, many countries use the US TLV system, with or without modifications. An account of the limits adopted is given in *Occupational Exposure Limits - World-wide* (Cook, 1987 AIHA/12).

18.6 Hygiene Standards: Occupational Exposure Limits

The system of occupational exposure limits (OELs) now used in the UK is described, as stated above, in EH 40/94 *Occupational Exposure Limits 1994* (HSE, 1994). Two sets of limits are used. These are (1) the maximum exposure limits (MELs) and (2) the occupational exposure standards (OESs). The difference between these two types of limit is that, whereas an OES is set at a level at which there is no indication of risk to health, for an MEL a residual risk may exist.

These occupational exposure limits are to be viewed in the context of the regulations governing occupational health, specifically the COSHH Regulations 1988 and the accompanying Approved Code of Practice ACOP L5 *Control of Substances Hazardous to Health and Control of Carcinogenic Substances* (HSE, 1988). These regulations are discussed in detail in Chapter 25, the discussion here being confined to the occupational exposure limits themselves.

18.6.1 Maximum exposure limits

A maximum exposure limit (MEL) is the maximum concentration, averaged over a reference period, to which an employee may be exposed by inhalation in any circumstances. MELs are listed in Schedule 1 of the COSHH Regulations 1988 and also in EH 40/94, which also give the reference periods.

There are two reference periods, a long-term period and a short-term period. The long-term period is an 8-hour time-weighted average (TWA) period. The short-term period given in EH 40/94 is 15 minutes. This is a recent change from a previous value of 10 minutes. Selected values of the MEL from EH 40/94 are given in Table 18.10, Section A.

18.6.2 Occupational exposure standards

As already stated, an occupational exposure standard (OES) is a concentration at which there is no indication of risk to health. OESs are listed in EH 40/94, which is referred to in the COSHH Regulations as the List of Approved OESs. The reference periods are the same as for the MELs, the long-term one being an 8-hour time weighted average and the short-term one being 15 minutes. Selected values of the OES from EH 40/94 are given in Table 18.10, Section B.

18.6.3 Occupational exposure limit system

MELs and OESs are set by the Health and Safety Commission (HSC) on the recommendations of the Advisory Committee on Toxic Substances (ACTS), following assessment by the Working Group on the Assessment of Toxic Chemicals (WATCH).

A substance is assigned an OES if it meets all three of the following criteria:

> Criterion 1: the available scientific evidence allows for the identification, with reasonable certainty, of a concentration averaged over a reference period, at which there is no indication that the substance is likely to be injurious to employees if they are exposed by inhalation day after day to that concentration; and
> Criterion 2: exposure to concentrations higher than that derived under criterion 1 and which could reasonably occur in practice, are unlikely to produce serious short- or long-term effects on health over the period of time it might reasonably take to identify and remedy the cause of excessive exposure; and
> Criterion 3: the available evidence indicates that compliance with the OES, as derived under criterion 1, is reasonably practicable.

A substance is assigned an MEL if it meets either of the following criteria:

> Criterion 4: the available evidence on the substance does not satisfy criterion 1 and/or 2 for an OES and exposure to the substance has, or is liable to have, serious health implications for workers; or
> Criterion 5: socio-economic factors indicate that although the substance meets criteria 1 and 2 for an OES, a numerically higher value is necessary if the controls associated with certain uses are to be regarded as reasonably practicable.

The setting of an OES proceeds, in principle, by identifying the critical health effect, determining a no observable adverse effect level (NOAEL) and determining a limit. Generally the data available are from animal experiments, and judgement has to be exercised with respect to confidence levels and extrapolations.

A substance is assigned an MEL only if there are serious health implications for workers, which may be serious effects for a small number of workers or less serious effects for a large number. Most substances to which MELs have been assigned are carcinogens or chemicals for which no threshold of effect can be identified and for which there is doubt about the seriousness of exposure.

In setting OESs account is taken of the indicative limit values given in EC Directive 91/332/EEC.

Synopses of the data used in setting limits are given in EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992), which is up-dated annually.

The units of measurement for OELs are as follows: for gases and vapours in air, either ppm or mg/m^3; for

airborne particles (fume, dust, etc.), mg/m^3; and for fibres, either mg/m^3 or fibres/ml. For dusts, limits are given as 'total inhalable' fraction unless specified as 'respirable' fraction.

The treatment of substances assigned an MEL under the COSHH Regulations, specifically Regulation 7(4), differs from that of those assigned an OES.

The lists of OESs and MELs are up-dated annually in EH 40. This publication also includes a table of new or revised entries in the list and a table showing substances which are under review.

18.6.4 Long- and short-term exposure limits

The basic OEL is the long-term, 8-hour time-weighted average limit, which is intended to control effects caused by prolonged or accumulated exposure. Where a substance has effects which occur after only a brief exposure, a short-term, usually 15-minute, limit is applied. Some substances have only a long-term limit, others have both a long-term and a short-term limit, and others again have only a short-term limit. Where a substance is governed by both types of limit, the short-term limit restricts the extent of any excursion above the average concentration during longer exposures. Where there is no short-term limit, EH 40 recommends that short-term excursions should not exceed three times the long-term limit. For some substances the effects of a brief exposure may be critical, and for these a short-term limit is used; a separate long-term limit is considered unnecessary and the short-term limit is applied throughout the shift. The period to which the limits apply are termed the reference periods, the periods being, as stated, 8 hours and 15 minutes for long- and short-term limits, respectively.

18.6.5 Application of occupational exposure limits

An MEL is a maximum limit. The long-term, 8-hour limit attracts requirements for monitoring under the COSHH Regulations, unless an assessment shows such monitoring to be unnecessary. The Regulations also require that the exposure of personnel be kept as far below this level as reasonably practicable. The short-term, 15-minute, MEL should never be exceeded.

Control to or below an OES can always be regarded as adequate under the COSHH Regulations. However, it is still incumbent on the occupier to follow good occupational hygiene practice and it is prudent to reduce exposure below the OES to allow for concentration fluctuations in the workplace. There are certain circumstances in which control may still be deemed adequate even if an OES is exceeded; these are described in Chapter 25.

18.6.6 Limitations of occupational exposure limits

OELs are intended to be used for normal working conditions in factories and other workplaces. Their application is not to be extended to other situations, and specifically they should not be used as limits either for emergencies or for pollution.

18.6.7 Mixed exposures

The majority of OELs are for individual substances, although a few relate to complex mixtures such as white spirit. In some situations workers are exposed to a mixture of substances. In some instances, an OEL for a mixture may be already established. In this case it can be used, but should it not be extrapolated to situations where the concentrations are different.

For mixtures, three different situations are recognized: (1) synergistic substances, where the presence of one substance causes another to produce a much greater toxic effect; (2) additive substances, where the effects of the substances are additive; and (3) individual substances, where there are no known or likely synergistic or additive effects.

Synergistic effects may arise because one substance enhances the toxicity of another, or because it potentiates the other, causing it to act in a qualitatively different way. Where effects are additive, EH 40 gives the following formula for the overall OEL:

$$L = \sum_{i=1}^{n} \frac{C_i}{L_i} \qquad L < 1 \qquad [18.6.1]$$

where C_i is the TWA of the ith component, L_i its OEL and L the overall OEL. Where effects are individual, it is sufficient to comply with each OEL separately.

It will be apparent that in many situations involving mixtures expert advice is required.

18.6.8 Skin effects

For certain substances there exists the hazard of absorption through the skin as well as by inhalation. EH 40 uses the skin notation 'Sk' against the substance in the lists. For these substances special precautions should be taken to prevent skin contact.

18.6.9 Sensitizer effects

Certain substances act as sensitizers in that they may cause sensitization of the respiratory tract if inhaled or of the skin if contact occurs. Respiratory sensitizers can cause asthma and other conditions, skin sensitizers cause allergic contact dermatitis. Individuals exposed may react even to minute amounts of the sensitizing substances. EH 40 uses the sensitizer notation 'Sen' against substances in the lists which are in certain defined categories and which have been identified as respiratory sensitizers. For these substances particular care should be taken to minimize airborne concentrations and to prevent their spread to other areas.

18.6.10 Asphyxiants

Some gases and vapours act as simple asphyxiants. They are hazardous insofar as they may reduce the oxygen content in the workplace. They include acetylene, argon, ethane, ethylene, helium, hydrogen, nitrogen, propane and propylene. Many of these substances are colourless and odourless and are thus not readily detected.

As the list just given shows, many asphyxiants are also flammable, and the concentration at which they present a fire or explosion hazard (the lower flammability limit) is generally lower than that at which they cause asphyxiation. It may be noted that many hydrocarbons are not classed as simple asphyxiants, but have an OEL value. Butane is one example.

Asphyxiants do not rank as substances hazardous to health for the purposes of the COSHH Regulations.

18.6.11 Carcinogens

As described earlier, some carcinogenic substances are prohibited. Other substances which have or may have

carcinogenic potential are listed in Appendix 9 of EH 40/94 and are assigned the 'Risk phrase' 'R45; may cause cancer' in the current edition of the *Authorised and Approved List: Information Approved for the Classification, Packaging and Labelling of Dangerous Substances for Supply and Conveyance by Road* (the *Approved List*).

Some substances listed in EH 40/94, Appendix 9, and assigned the 'Risk phrase' are given an MEL. They include acrylonitrile, benzene, ethylene oxide and vinyl chloride. Other substances are simply listed in the appendix.

Guidance on carcinogens under the COSHH Regulations is given in the second of the two ACOPs in L5 *Control of Substances Hazardous to Health and Control of Carcinogenic Substances* (HSE, 1988).

18.6.12 Dusts

For dusts a distinction is made between 'total inhalable dust' and 'respirable dust'. The former approximates to the fraction of the airborne material which enters the mouth and nose during breathing and is therefore available for deposition in the respiratory tract. The latter refers to the fraction which penetrates to the gas exchange region of the lung. Details are given in MDHS 14 *General Method for the Gravimetric Determination of Respirable and Total Inhalable Dust* (HSE, 1989). Some dusts are assigned an OEL. EH 40/94 gives OELs for a number of dusts, including grain dust and silica (crystalline), which have an MEL, and emery, graphite, limestone, silica (amorphous) and starch, which have an OES. Dust of crystalline silica, or quartz, is of particular importance as the cause of silicosis and attracts a low OEL. It has an long-term MEL for the respirable dust of 0.4 mg/m^3.

The former TLV system used in the UK identified some dusts as toxic and assigned a TLV, but treated other dusts as nuisance dusts, which were not considered toxic, although they could be unpleasant to breathe and could cause irritation by abrasive action.

In the current system there are dusts which do not attract an OEL. EH 40/94 states that in the absence of a specific limit and of any indication for the need for a lower limit, exposure should be controlled below 10 mg/m^3 for an 8-hour TWA. A concentration at this level or above is to be taken as a 'substantial concentration' for the purposes of Regulation 2 of the COSHH Regulations and as rendering the dust a substance hazardous to health under those regulations.

18.6.13 Asbestos

Asbestos is controlled by the Control of Asbestos at Work Regulations 1987 (CAWR). It is considered in Section 18.8.

18.6.14 Lead

Lead is controlled by the Control of Lead at Work Regulations 1980, which is complemented by COP2 *Control of Lead at Work* (HSE, 1985). The lead-in-air standards given in this ACOP, and in EH 40/94, are as follows. The 8-hour TWA (as Pb) is 0.15 mg/m^3 for lead and lead compounds other than tetraethyl lead, and 0.10 mg/m^3 for tetraethyl lead.

18.6.15 Working conditions

In applying OELs regard should be had to working conditions that may impose additional stress and may enhance toxic effects. These include exposure to high temperature, high humidity or UV radiation.

18.7 Carcinogens

18.7.1 Cancer risk

There are a number of accounts of the contribution of cancer to mortality. They include *The Causes of Cancer* (Doll and Peto, 1981) and other treatments by Doll (1979), Peto (1979), A.E.M. (McLean 1979) and (Higginson 1984).

As infectious diseases have declined as a cause of death, the proportion of deaths attributable to cancer has tended to rise. Cancer is now a major cause of death. In developing countries it accounts for some 20% or more of deaths. This is also the case for the UK and the USA. The numbers of people who die of cancer are therefore large. In 1980, in England and Wales, the number of deaths from cancer was 130 000 and the proportion 22%. In 1977, cancer caused 382 000 deaths in the USA.

The factors that cause cancer are physical, biological and cultural as well as chemical. Two of the principal factors are cultural. One of these is smoking, which is perhaps the most generally accepted major cause of cancer. There is also strong evidence that diet is another major cause. Estimates of the proportions of avoidable cancers given by Higginson and Muir (1979) in a case study done in England are given in Table 18.11, together with figures quoted by Doll and Peto (1981) in a study done in the USA.

The trend in cancer mortality has been reviewed by Doll (1979), who found that over the 40-year period 1931–35 to 1971-75, for 26 sites in the male body and 28 sites in the female body, the age standardized mortality at 45–64 years of age showed less than 1% variation at 25 sites, a progressive decrease of more than 1% at 16 sites and a progressive increase of more than 1% at 13 sites. He concludes that where increases in cancer rates have occurred this is due mainly to personal and dietary habits rather than to exposure to chemicals.

Table 18.11 *Estimates of the proportion of avoidable cancers*[a] *(after Higginson and Muir, 1979)*

Feature	*Proportion of avoidable deaths (%)*	
	Male	*Female*
Tobacco	30	7
Alcohol	5	3
Life-style	30	63
Occupation	6	2
Iatrogenic	1	1
Geophysical	11	11
Congenital	2	2
Unknown	15	11

[a] Figures given by Doll and Peto (1981) for the USA include the following proportions for both sexes: tobacco 30%; alcohol 3%; life-style 42%; infection 10%; and occupation 4%.

Table 18.12 *Estimates of cancer deaths attributable to occupational exposure (after US Congress, Office of Technology Assessment, 1981)*

	Preferred estimate (%)	*Period to which estimate applies*	*Reference*
Male incidence, USA	4	1976	Wynder and Gori (1977)
Female incidence, USA	2	1976	
Male cancer, England	6	1968–72	Higginson and Muir (1979)
Female cancer, England	2	1968–72	
Male mortality, USA	6.8	1977	Doll and Peto (1981)
Female mortality, USA	1.2	1977	

The proportion of cancer deaths which are attributable to occupational exposure, which includes exposure to chemicals at work, is estimated by many authorities as about 5%. In this respect the estimates given in Table 18.12 are typical. A review of these estimates has been given by Corn and Corn (1984).

This view is strongly disputed by certain workers, who believe that the contribution of chemicals, in the workplace, in food and in the environment, is underestimated by 'establishment' workers, and they represent a 'radical' view. Statements of this viewpoint are given in *The Politics of Cancer* (S.S. Epstein, 1978) and *Cancer In Britain. The Politics of Prevention* (Doyal and Epstein, 1983). It is argued by these workers that exposure to chemicals may account for some 40% of cancer deaths.

These critics (e.g. S.S. Epstein, 1978) argue that there is a tendency to estimate the proportion of cancers attributable to chemicals as the residue remaining after estimates have been made of those attributable to other causes and that this approach is unsound. On the other hand, it is argued (e.g. Peto, 1980) against these critics that they tend to make their estimates of potential cancer mortality from a particular chemical by combining the numbers exposed to any level of the chemical with the risk attributable to persons exposed to very high levels.

The authors of the *Health and Safety Statistics 1990-91* (HSE, 1992b) discuss the number of premature deaths from cancer. On the basis of the work of Doll and Peto it might be estimated that about 4% of cancers are work-related, which would give some 5000 premature deaths. A death from cancer might be avoided by the removal of any one of a number of contributing factors, of which workplace exposure is only one. The only hard statistics given are that there were some 78 cases of awards for occupational cancer other than mesothelioma (from asbestos).

18.7.2 Regulatory controls in Europe

The Sixth Amendment to the EC Directive on Dangerous Substances (79/831/EEC) creates controls on the introduction of new chemicals and thus of potential carcinogens. There is, in addition, a specific Directive which deals with carcinogens (90/394/EEC).

There is also an ILO Convention on Carcinogenic Substances and Agents. An account of the European arrangements for the regulation of carcinogens is given by Rijkels (1984).

18.7.3 Regulatory controls in the UK

The Carcinogenic Substances Regulations 1967 prohibit the use of certain human carcinogens and the Carcinogenic Substances (Prohibition of Importation) Order 1967 prohibit their importation.

As stated earlier, the COSHH Regulations 1988 cover carcinogens. HSE guidance is given in the associated ACOP L5 *Control of Substances Hazardous to Health and Control of Carcinogenic Substances* (HSE, 1988). The occupational exposure limits are given in EH 40/94 *Occupational Exposure Limits 1994* (HSE, 1994). Carcinogens are one of the categories of substance given in the MEL list.

The control of one particular important carcinogen, asbestos, is effected through the Control of Asbestos at Work Regulations 1987.

18.7.4 Regulatory controls in the USA

In the USA the framework legislation for the control of carcinogens, as for other toxic chemicals, is the Occupational Safety and Health Act 1970 administered by OSHA, but other legislation of particular relevance is the Toxic Substances Control Act 1976 administered by the EPA. The control of carcinogens in the workplace is effected through the system of standards set by the OSHA.

The standards which may now be adopted are constrained by the results of the Benzene Case and the Formaldehyde Case, described above. Between 1977 and 1980, the OSHA attempted in the document *Identification, Classification and Regulation of Occupational Carcinogens* (OSHA, 1977) to set a generic standard for carcinogens. The Benzene Case increased the difficulty of creating such a standard and a generic standard was not adopted.

18.7.5 Carcinogenic chemicals

Some information on the toxicity of carcinogens is given in works on the toxicity of chemicals in general, of which carcinogenic chemicals are a subset, but there are also a number of specific treatments. Accounts of carcinogenic substances are given in *Cancer Causing Chemicals* (Sax, 1981), *Carcinogenically Active Chemicals: A Reference Guide* (Lewis, 1991 ACGIH/53) and *Handbook of Toxic and Hazardous Chemicals and Carcinogens* (Sittig, 1991 ACGIH/59).

Table 18.13 *OSHA list of carcinogens for airborne concentrations 1980*

2-Acetylaminofluorene[a]	3,3-Dichlorbenzidine[a]
Acrylonitrile[a]	4-Dimethylaminoazobenzene[a]
4-Aminodiphenyl[a]	Ethyleneimine[a]
Arsenic[a]	4,4-Methylene-bis(2-chloronile)
Asbestos[a]	β-Naphthylamine[a]
Benzene[a]	Nickel (and salts)
Benzidine[a]	4-Nitrobiphenyl[a]
Bis(chloromethyl)ether[a]	*N*-Nitrobiphenyl[a]
Chromic acid and chromates[b]	Propiolactone[a]
Coke-oven emissions[a]	Soots, tars, and mineral oils
1,2-Dibromo-3-chloropropane	Vinyl chloride[a]

[a] Permanent standards promulgated after Administrative Procedures Act rule-making.
[b] From the ANSI list.

The identification of chemicals which are carcinogenic is one of the main tasks of the International Agency for Research on Cancer (IARC). By 1979 the IARC (1979a) had identified 16 chemicals and industrial processes, as well as soot and vinyl chloride, for which there is sufficient epidemiological evidence to indicate a link between exposure and excess cancer in man. It has also identified a further 18 chemicals which the epidemiological evidence indicates as being probable human carcinogens.

According to Corn and Corn (1984), there are some 350 chemicals which are suspected of being human carcinogens. A list of carcinogens regulated by the OSHA for airborne concentrations in 1980 is given in Table 18.13.

18.7.6 Benzene

Benzene is an important chemical in the petroleum and petrochemical industries and the numbers of people who have been exposed to it in some degree is large. For many years it was regarded as not particularly toxic. The attitude to exposure both in industry and in laboratories was relatively relaxed. More recently the long-term effects of benzene on the blood and bone marrow and its carcinogenic properties have been better appreciated and the hygiene limits have been greatly reduced.

Reviews of toxicity are given in *Criteria Document* Publ. 74-137 *Benzene* (NIOSH, 1974), TR 4 *Toxicity Review: Benzene* (HSE, 1982), *Benzene: Occupational and Environmental Hazards* (Mehlman, 1989 ACGIH/28) and EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992).

The development of controls on benzene is described by Thorpe (1978a,b) and by Barnard (1984). The following extracts from a table by Thorpe (1978a) illustrate the tightening of exposure standards in the USA:

Year	*Limit* (ppm)	*Standard*
1946	100 ppm	ACGIH TLV
1947	50 ppm	ACGIH TLV
1957	25 ppm	ACGIH TLV-TWA
1963	25 ppm	ACGIH TLV-ceiling
1969	10 ppm	ANSI TLV-TWA, with ceiling of 25 ppm
1976	1 ppm	OSHA (proposed) with 5 ppm excursion

The HSE paper reviews the toxicity of benzene and micro-organism tests, animal experiments and epidemiological data. Benzene affects the formation of blood cells in bone marrow. It may reduce the number of red cells, white cells or platelets, or all three. It may cause anaemia or leukaemia.

Although in all three types of toxicity investigation there are many studies which have given negative results, some have demonstrated injurious effects. Carcinogenic, mutagenic and teratogenic effects have all been demonstrated for benzene in animal experiments. The review describes a number of epidemiological studies of workers exposed to benzene. A study by Infante *et al.* (1977a,b) of 748 workers on rubber film in Ohio found a significant increase in leukaemia. The authors quote low levels of exposure, below 15 ppm in most cases, but have apparently subsequently accepted that the levels may have been 100 ppm or more. Another study in which a significant increase in leukaemia was found is that by Pagnotto, Elkins and Brugsch (1979) on 549 workers at a Dow Chemical plant in the USA with very low exposures, about 2 ppm, but the workers concerned had a varied history of exposure to chemicals and there was no significant increase in leukaemia among other workers exposed to higher concentrations. Other studies which either are inconclusive or have shown no significant increase in leukaemia include those by Thorpe (1974) on 38 000 workers exposed to petroleum products, and Rushton and Alderson (1981) on 35 000 oil refinery workers.

The HSE review concludes that there is considerable evidence that exposure to high concentrations of benzene may eventually cause leukaemia, but that there is no conclusive evidence of leukaemia in workers exposed to lower concentrations. The only work reviewed in which there was an increase in leukaemia among workers exposed to less than 100 ppm was the Dow Chemical study just described. Increasing awareness of the toxicity of benzene has led to a progressive reduction in the hygiene limits. This is illustrated by the data given earlier. There has also been a corresponding tightening of the regulatory controls. As described above, in the USA this led to the attempt by the OSHA to introduce a very low benzene standard and the rejection of this by the courts in the Benzene Case. In the UK benzene has a long-term MEL of 5 ppm.

18.7.7 Vinyl chloride

Vinyl chloride monomer (VCM) is manufactured on a large scale and polymerized to give polyvinyl chloride (PVC), which is one of the most common plastics. It has a boiling point of -13°C and therefore is a gas at ambient temperatures.

Accounts of the toxicity of vinyl chloride are given in *Criteria Document* Publ. 78-205 (NIOSH, 1978), EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992), and in the other references quoted below.

Until the mid-1970s, vinyl chloride was regarded as a mild narcotic less harmful than chloroform. The ACGIH TLV was 500 ppm and the UK TLV was 200 ppm (HSE, 1972 TDN 2/72).

It was also well known that vinyl chloride could give rise to acro-osteolysis, which involves deterioration of the bones, particularly the fingers, and certain other conditions. These diseases have been found mainly in PVC workers in circumstances where the exposure may well have been at concentrations appreciably above 1000 ppm. However, in 1974 it was found, that vinyl chloride is a carcinogen.

Accounts of the development of the vinyl chloride problem are given in the *Annual Report of HM Chief Inspector of Factories 1974* (HMFI, 1974) and by Atherley (1978), Doyal and Epstein (1983) and Corn and Corn (1984).

Indications of the carcinogenicity of vinyl chloride were given by animal experiments conducted by Viola (1970), but the first widespread impact was made by a report from a BF Goodrich plant in the USA that three cases of a rare liver cancer, angiosarcoma, had been discovered and were probably associated with exposure to high levels of vinyl chloride. The men concerned had been autoclave cleaners in plant polymerizing vinyl chloride to PVC. The average time for the condition to develop after first exposure was 19 years.

It is noteworthy that the cancer associated with vinyl chloride is a rare one. The discovery of a carcinogenic effect could have been much more difficult if the cancer had been of a type which also has other causes, such as the lung cancer which can be caused by cigarette smoking. It is probably fair to say that this discovery has had as great an impact in the area of chronic toxic exposure as the Flixborough disaster has had in the area of fire and explosion.

By the end of 1974, some 25 cases of angiosarcoma in workers exposed to vinyl chloride had been established world-wide. These were mostly in the USA and mostly in one company.

In the USA, the OSHA reduced the standard from 500 ppm to an interim standard of 50 ppm and then to a TLV of 1 ppm and a maximum of 5 ppm. It was envisaged, however, that it might be necessary to rely on the extensive use of respirators to meet these levels of exposure.

In the UK, the HSE issued *Vinyl Chloride Code of Practice for Health Precautions* (HSE, 1975b), which gave as an interim standard a TLV of 25 ppm and a maximum of 50 ppm.

Guidance to industrial users of the monomer was given in *Vinyl Chloride Monomer. Advisory Notes for PVC Processors* (BCISC, 1974/14). Notes on best practicable means for PVC polymer plants were given in the *Annual Report on Alkali, etc. Works 1974*. The publication *Vinyl Chloride and You* was issued to workers.

The monitoring of very low concentrations of vinyl chloride requires sensitive analytical methods. In the 1970s there was intense activity in this area. Methods of analysis were described in *The Determination of Vinyl Chloride–A Plant Manual* (CIA, 1975/7).

Various other countries adopted very low standards for vinyl chloride. The UK approach was based on the argument that it is preferable to devote effort to reducing the concentration of vinyl chloride in the atmosphere by improved engineering than to rely on respirators, which may well not be used.

The reduction of concentrations of vinyl chloride to very low levels is a difficult engineering problem. Early experience was that it was more difficult to eliminate occasional peaks over 50 ppm than to achieve the TWA of 25 ppm.

A survey of the atmospheric concentrations of vinyl chloride at plants in the UK was made in 1974 by the CIA (quoted by McKinnon (1974)). The survey established that the approximate exposure levels in the plant atmosphere were:

	Explosure level (ppm)
Plants polymerizing VCM to PVC	50
Plants producing VCM	5
Plants fabricating PVC	0–5

The survey obtained the following figures for the weekly average gas concentration in the seven polymerization plants in the UK:

Plant	*Weekly average concentration* (ppm)
A	25
B	10
C	10
D	25
E	20
F	40
G	30

The CIA stated that the ultimate for most existing plants is 10 ppm and that entirely new plants with the most modern techniques might achieve 5 ppm.

Accounts are also available of measures taken at that time to reduce exposure at plants in the USA and elsewhere (e.g. Chementator, 1975 Apr. 14, 33; Jul. 7, 34; 1977, Jan. 3, 37). Indications were that the achievement of low levels of exposure did not prove as difficult as was sometimes anticipated (e.g. Meade and Press, 1977).

Information on plant emissions of vinyl chloride has been given by Sittig (1978), who quotes vent and fugitive emission rates. The development of controls on vinyl chloride in the USA may be followed through the references given in Table A1.4.

In the UK vinyl chloride has a long-term MEL of 7 ppm with an overriding annual MEL of 3 ppm.

18.7.8 Acrylonitrile

In 1977, several animal and epidemiological studies were published which showed carcinogenic effects from acrylonitrile. One of these was an epidemiological study

by Dupont on 470 workers in an acrylic fibre plant in South Carolina, which showed the incidence of excess cancers.

As described by Karrh (1984), the company made its data, interpretation and recommendations available to the OSHA which accepted these and based a standard on them. The standard set by the OSHA was 2 ppm. This case is therefore an interesting example of co-operation between industry and the regulatory authorities. The author adds that, to his knowledge, this is the only OSHA health standard which has not been the subject of litigation.

In the UK, the practicality of the 2 ppm standard was a matter of some debate, but by 1981 this level was accepted, as described by Doyal and Epstein (1983). Acrylonitrile now has a long-term MEL of 2 ppm.

18.7.9 Other substances

Other substances with carcinogenic potential include bis(chloromethyl) ether (BCME), formaldehyde, inorganic arsenic and asbestos.

For BCME the toxicity and development of controls are described Doyal and Epstein (1983) and by Kusnetz and Lynch (1984).

Chloromethyl ether (CME) is manufactured by reacting formaldehyde and hydrogen chloride. BCME is an intermediate and a contaminant in the CME. BCME has long been known to be a highly toxic irritant gas, but awareness of its carcinogenic properties dates from various epidemiological and animal studies done in the 1960s and 1970s. In 1982, the ACGIH classified BCME as a carcinogen. In the UK BCME has a long-term MEL of 0.001 ppm.

For formaldehyde a review of toxicity is given in TR2 *Toxicity Review: Formaldehyde* (HSE, 1981). The toxicity and the development of controls on formaldehyde are described by Neal and Gibson (1974), Doyal and Epstein (1983), Barnard (1984), and Gough (1984).

Formaldehyde has been shown to be carcinogenic to rodents, but there is disagreement among experts on the extent of its human carcinogenicity. In the Formaldehyde Case the CPSC used some of the animal experiments and interpretations in support of its ban on urea formaldehyde insulation, but its assessment was not accepted by the court. Following a further expert review under the aegis of the National Center of Toxicological Research (NCTR), the OSHA decided not to alter its standard for formaldehyde. In the UK, formaldehyde has long- and short-term MELs which are both 2 ppm.

For inorganic arsenic the toxicity and development of controls are described by Lowrance (1984), Neal and Gibson (1984) and Sagan and Whipple (1984). There is epidemiological evidence of the human carcinogenicity of inorganic arsenic (OSHA, 1983). In 1983, on the basis of this evidence, the OSHA adopted a standard of 10 $\mu g/m^3$. As described above, the reasoning given by the OSHA in support of this standard, though not necessarily the numerical values, is commended by Lowrance (1984) as a model. In the UK, inorganic arsenic has a long-term MEL of 0.1 mg/m^3.

Asbestos is a carcinogenic dust and is considered in Section 18.8.

18.8 Dusts

There are many industrial chemicals which are used in powder form and can give rise to dust in the atmosphere. Dust may also be generated by the attrition of materials.

Dusts are covered by the OEL system, and OELs for dusts have been described in Section 18.6.

Some dusts are not classified as having any specific toxic effect, but can cause irritation. Excessive quantities of such dust are unpleasant to inhale, can deposit in the eyes and ears, and can injure the skin or mucous membranes by chemical or mechanical action or through the cleaning procedures necessary to remove them.

Other dusts can cause injurious effects. One such dust is silica in the crystalline, or quartz, form. A well known example is the silica dust produced in coal mining, which causes pneumoconiosis, a progressive fibrosis of the lung tissue.

Fibrosis can also be caused by asbestos dust. In addition, this dust is a carcinogen. Asbestos is considered in more detail below.

Metal dusts which are sufficiently fine can enter the lungs and give rise to the toxic symptoms associated with the parent metal.

Other dusts which are themselves non-fibrogenic may produce an allergic response in the lungs which leads eventually to fibrosis. Such conditions are 'farmer's lung' and byssinosis, an asthmatic condition prevalent in the cotton industry. Process workers involved with enzyme washing powders have experienced similar asthmatic conditions.

The control of dust in the workplace is considered in Chapter 25.

18.8.1 Asbestos

'Asbestos' is a generic term which is applied to a number of naturally occurring, hydrated mineral silicates. More than 90% of the world production of asbestos is as is chrysotile ('white') asbestos. Virtually all the rest is amosite ('brown') and crocidolite ('blue') asbestos.

Accounts of the toxicity of asbestos include *Criteria Document* Publ. 77-169 *Asbestos* (NIOSH, 1977), *Asbestos: Medical and Legal Aspects* (Castleman, 1990 ACGIH/39), EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992) and the other references quoted below. Other HSE publications on asbestos are given in Chapter 25.

Asbestos has been in widespread use as a material for building products, fireproofing, lagging, brakes, glands and many other purposes. Asbestos dust is generated to some degree in many of these applications, particularly in cutting and demolition operations.

There are two injurious effects caused by asbestos dust, the fibres of which enter the lung. One is asbestosis, a fibrosis of the lung. The other is mesothelioma, a rare cancer of the lung and bowels, of which asbestos is the only known cause.

Evidence of the hazard of asbestos appeared as early as the 1890s. Of the first 17 people employed in an asbestos cloth mill in France, all but one were dead within 5 years. Oliver (1902) describes the preparation and weaving of asbestos as 'one of the most injurious processes known to man'.

In 1910, the Chief Medical Inspector of Factories, Thomas Legge, described asbestosis. A high incidence of lung cancer among asbestos workers was first recognized in the 1930s and has been the subject of continuing research. The synergistic effect of cigarette smoking, which greatly increases the risk of lung cancer to asbestos workers, was also discovered (Doll, 1955). The specific type of cancer, mesothelioma, was identified in the 1950s (J.C. Wagner, 1960).

In the UK, an Act passed in 1931 introduced the first restrictions on the manufacture and use of asbestos. It has become clear, however, that the concentrations of asbestos dust allowed by industry and the Factory Inspectorate were too high. In consequence, numbers of people have been exposed to hazardous concentrations of the dust over long periods.

The problem was dramatically highlighted by the tragedy of the asbestos workers at Acre Mill, Hebden Bridge. The case was investigated by the Parliamentary Commissioner (Ombudsman) (1975–76). It was found that asbestos dust had caused disease not only to workers in the factory but also to members of the public living nearby.

Although all types of asbestos can cause cancer, it is held that crocidolite, or blue asbestos, is the worst offender.

By the late 1960s, growing concern over the asbestos hazard in the UK led to action. The building industry virtually stopped using blue asbestos in 1968 and the Asbestos Regulations 1969 prohibited the import, though not the use, of this type of asbestos.

The problem of asbestos continued to be a subject of controversy (e.g. Kinnersley, 1976; W.P. Howard, 1976). Criticisms included the failure of industry and government to act earlier, the adequacy of current concentration standards, the particular hazard of blue asbestos, and the effect of 'casual' exposures. Obviously the problem is more difficult if it is not confined to blue asbestos and if even occasional exposure can cause cancer.

Most cases of disease from asbestos are associated with exposure over a period of years and often in high dust concentrations, but several cases have been quoted of contraction of the cancer after apparently very short exposure. However, in some of these at least, it has been shown that the exposure, though short, was in fact quite intense.

As a result of continuing concern, in 1976 the Government set up an Advisory Committee on Asbestos (ACA). The asbestos industry also set up its own Asbestos Advisory Committee. In contrast to most of the other chemicals discussed earlier, and in particular to vinyl chloride monomer, asbestos is a material widely used by the public. The industry was therefore faced with the problem of allaying the fears of numerous and relatively unsophisticated users.

The Asbestos Regulations 1969 were followed by further legislative requirements. These include The Asbestos (Licensing) Regulations 1983 and the Asbestos (Prohibition) Regulations 1985.

The Control of Asbestos at Work Regulations 1987 (CAWR), which revoke the Asbestos Regulations 1969, now provide a comprehensive set of controls on asbestos. The corresponding ACOP is L27 *The Control of Asbestos at Work* (HSE, 1988).

The CAWR 1987 set control limits for asbestos. These limits are reproduced in EH 10 *Asbestos – Exposure Limits and Measurement of Airborne Dust Concentrations* (HSE, 1990) and in EH 40/94. They are given in Chapter 25 where the CAWR 1987 are discussed in more detail. A more stringent limit is applied for crocidolite or amosite asbestos.

Although there is now much more stringent control of asbestos dust, the backlog of exposure in previous years is likely to claim victims for some time to come. The *Health and Safety Statistics 1990-91* (HSE, 1992b) give, for 1990, 882 deaths recorded as due to mesothelioma and another 163 deaths recorded as due to asbestosis (excluding those where mention is made of mesothelioma).

18.8.2 Dust and fume atmospheres

Not infrequently, dusts occur as part of a mixture of dusts, fumes, gases and vapours. This is the situation, for example in ferrous foundries. A recent review of airborne ferrous foundry particulates (HSE, 1994a) has highlighted the enhanced risk of lung cancer from such atmospheres.

18.9 Metals

The toxic effects of metals and their compounds vary according to whether they are in inorganic or organic form, whether they are in the solid, liquid or vapour phase, whether the valency of the radical is low or high and whether they enter the body via the skin, lungs or alimentary tract.

Some metals which are harmless in the pure state form highly toxic compounds. Nickel carbonyl is highly toxic, although nickel itself is fairly innocuous. The degree of toxicity can vary greatly between inorganic and organic forms. Mercury is particularly toxic in the methyl mercury form.

The wide variety of toxic effects is illustrated by the arsenic compounds. Inorganic arsenic compounds are intensely irritant to the skin and bowel lining and can cause cancer if exposure is prolonged. Organic compounds are likewise intensely irritant, produce blisters and damage the lungs, and have been used as war gases. Hydrogen arsenic, or arsine, is non-irritant, but attacks the red corpuscles of the blood, often with fatal effects.

Hazard arises from the use of metal compounds as industrial chemicals. Another frequent cause of hazard is the presence of such compounds in effluents, both gaseous and liquid, and in solid wastes. Fumes evolved from the cutting, brazing and welding of metals are a further hazard. Such fumes can arise in the electrode arc welding of steel. Fumes which are more toxic may be generated in work on other metals such as lead and cadmium.

The HSE has issued a number of *Guidance Notes* on metals and their hazards, including notes on cadmium (EH 1), chromium (EH 2), arsenic (EH 8), beryllium (EH 13), mercury (EH 14), antimony (EH 17) and lead (EH 29). There are also notes on the compounds arsine (EH 11), stibine (EH 12) and phosphine (EH 20).

18.9.1 Lead

One of the metals most troublesome in respect of its toxicity is lead. Accounts of the toxicity of lead are given in *Criteria Document* Publ. 78-158 *Lead, Inorganic* (NIOSH, 1978) and EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1992).

The toxicity of lead and its compounds has been known for a long time, since it was described in detail by Hippocrates. Despite this, lead poisoning continues to be a problem, particularly where cutting and burning operations, which can give rise to fumes from lead or lead paint, are carried out. Fumes are emitted above about 450–500°C. These hazards occur in industries working with lead and in demolition work.

Legislation to control the hazard from lead includes the Lead Smelting and Manufacturing Regulations 1911, the Lead Compounds Manufacture Regulations 1921, and the Lead Paint (Protection against Poisoning) Act 1926 and the Control of Lead at Work Regulations 1980. The associated ACOP is COP 2 *Control of Lead at Work* (HSE, 1988).

The limits for lead, which is referred to as the 'lead-in-air standard', are given in COP 2 and in Appendix 5 of EH 40. They have been given in Section 18.6.

Monitoring of lead in the working environment is dealt with in EH 28 *Control of Lead: Air Sampling Techniques and Strategies* (HSE, 1986).

The *Annual Report of HM Chief Inspector of Factories 1974* records 36 cases of lead poisoning in that year. Also, 154 employees were removed from lead work because of increased lead absorption. The number of cases of lead poisoning was 82 in 1972 and 59 in 1973. The *Health and Safety Statistics 1990–91* (HSE, 1992b) do not quote cases of lead poisoning but the statistics given show that in 1990–91 some 258 male workers and 26 female workers were suspended from work due to the levels of lead in their blood.

18.9.2 Mercury

Another highly toxic substance is mercury. This is used on a large scale in the chemical industry in the manufacture of chlorine by the mercury cell process.

Mercury is particularly toxic in the organic form, and especially as methyl mercury. Organic mercury was responsible for the tragedy at Minimata, Japan, where many members of the public were poisoned and deformed by liquid effluent containing mercury.

Mercury vapour from spillage of the metal should also be treated as hazardous.

Industrial use of mercury is dealt with in EH 17 *Mercury – Health and Safety Precautions* (HSE, 1977).

18.10 Emergency Exposure Limits

Limits for occupational exposure are complemented by limits for emergency exposure. A number of types of limit for exposure in an emergency have been defined by various bodies, but it is fair to say that there is no system with a status comparable to that of the TLV or OEL systems.

Some emergency exposure limits, emanating from various bodies, include the following:

EEGL	Emergency Exposure Guidance Level
EEI	Emergency Exposure Index
EEL	Emergency Exposure Limit
ERPG	Emergency Response Planning Guideline
IDLH	Immediately Dangerous to Life and Health (limit)
PEEL	Public Emergency Exposure Limit
SPEGL	Short-Term Public Emergency Guidance Level

The National Research Council (NRC) Committee on Toxicology has, since the 1940s, submitted to the Department of Defense EEGLs for toxic chemicals. An EEGL is a concentration which is judged acceptable and which will permit exposed individuals to perform specified tasks during emergency conditions lasting from 1 to 24 hours. The NRC has also developed SPEGLs. These are acceptable concentrations for exposures of members of the general public. Some early limits were those given in the *Guides for Short Term Exposure of the Public to Air Pollutants* (NAS/NRC, 1972a, 1973). More recent publications are the *Guidance Levels for Emergency and Continuous Exposure to Selected Airborne Contaminants* (NAS, 1984–).

A number of EELs were developed in the early 1970s in the Netherlands, as described by the Committee for the Prevention of Disasters (CPD) in the Netherlands (1974) and by Zielhuis (1970), Siccama (1973) and Balemans (1975).

The National Institute for Occupational Safety and Health (NIOSH) has published a set of IDLH limits. NIOSH data are given in the *Pocket Guide to Chemical Hazards* (NIOSH, 1990/18).

The American Industrial Hygiene Association (AIHA) publishes a series *Emergency Response Planning Guidelines* (AIHA, 1988–/13). An ERPG is the maximum airborne concentration below which, it is believed, nearly all individuals could be exposed for up to 1 hour without experiencing or developing certain defined effects. Three ERPGs are used, the defined effects being as follows:

ERPG-1	Effects other than mild transient adverse health effects or perception of a clearly defined objectionable odour.
ERPG-2	Irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.
ERPG-3	Life threatening health effects.

So far some 40 ERPGs have been published. The ERPG-2 is broadly similar to the EEGL.

Another emergency limit is the EEI given in *Emergency Exposure Indices for Industrial Chemicals* (ECETOC, 1991). Three EEIs are defined, namely EEI-1, EEI-2 and EEI-3, which separate four zones of effect: detection, discomfort, disability, and permanent incapacity/death.

Another limit used is the PEEL. This is a maximum airborne concentration to which a member of the public may be exposed without significant adverse effects.

Critical reviews of emergency exposure limits are given in the *QRA Guidelines* (CCPS, 1989/4) and by Franklin (1991).

18.10.1 Dow Chemical Exposure Index

There are also indices for acute toxic exposures which are not a simple concentration value, but take account of other parameters also. One such is the Chemical Exposure Index (CEI) developed by the Dow Chemical

Company (1994a) and described by R.A. Smith and Miller (1988).

The CEI takes account of (1) toxicity, (2) quantity, (3) distance, (4) molecular weight, and (5) process variables, and the index is computed as the product of a set of 'scale factors' which allow for these features. The authors give full details, including proformas and credit factors.

18.11 Gas Toxicity

18.11.1 Industrial gases

Some of the principal toxic gases which are handled in the chemical industry and the toxic effect which each exerts are:

Gas	*Toxic effect*
Ammonia	Irritant
Bromine	Irritant
Chlorine	Irritant
Hydrogen chloride	Irritant
Hydrogen cyanide	Systemic
Hydrogen fluoride	Systemic (fluoride poisoning), irritant
Hydrogen sulphide	Systemic, irritant
Phosgene	Irritant
Sulphur dioxide	Irritant

All except one of these gases are irritants. In this context 'irritation' is a technical term: the effect ranges from mild discomfort to death. An irritant gas attacks the respiratory tract and the lungs. The locus of action depends mainly on the solubility of the gas, the more soluble gases attacking the respiratory tract and the less soluble the lungs. The action of irritant gases has been described by Haggard (1924) as follows:

> Ammonia produces intense congestion of the upper respiratory passages and immediate death from laryngeal spasm or oedema; on the other hand phosgene and nitrogen peroxide cause little irritation of the upper respiratory tract but induce pneumonia or lung oedema through their action upon the lung alveoli; chlorine in its action is intermediary between ammonia on the one hand and phosgene and nitrogen peroxide on the other.

Of the irritant gases, ammonia and hydrogen fluoride are miscible with water. Bromine is more soluble than chlorine which is turn is more soluble than phosgene. As indicated, ammonia and hydrogen fluoride attack the upper respiratory tract. The main action of chlorine is on the lungs, but there is some effect on the respiratory tract. Bromine, being more soluble than chlorine but less soluble than ammonia, attacks both the respiratory tract and the lungs. Phosgene, being less soluble than chlorine, enters deep into the lungs where its action occurs.

Hydrogen sulphide is an irritant gas, but also attacks the nervous system and causes respiratory paralysis. It is oxidized in the blood stream to pharmacologically inert compounds. Hydrogen fluoride is again an irritant gas but also gives rise to fluoride poisoning in the body.

Hydrogen cyanide is the only one of the gases listed which is not an irritant; it causes cyanide poisoning. The most important effect of this is probably the inhibition of cytochrome oxidase, which in turn prevents the utilization of molecular oxygen by the cells. The cyanide is excreted in the urine.

18.11.2 Lethal concentration and load

In general, the injurious effect of the inhalation of a toxic gas is a function of concentration and of time which may be expressed by the relation

$$c^n t^m = \text{Constant} \qquad [18.11.1]$$

where c is the concentration, t is the time, and m and n are indices.

If the exposure time is constant, a lethal concentration LC_i may be defined such that for this exposure time C_i is the concentration which is lethal at the i% level. Widespread use is made of the LC_{50} value and also of other values such as LC_{10}, LC_{05} and LC_{01}.

If the exposure time is not constant, but the injurious effect is proportional to the product ct of the concentration and time ($m = n = 1$), and hence to the dosage D, a lethal dosage LD_i may be defined with

$$D = ct \qquad [18.11.2]$$

If the injurious effect is proportional to some other function ($m \neq n$), it is necessary to use the concept of toxic load L and to define a lethal load LL_i with

$$L = ct^m \qquad [18.11.3]$$

An alternative toxic load, L^* may also be defined

$$L^* = c^n t \qquad [18.11.4]$$

with $m = 1/n$. This second form of the lethal load is that most often used in hazard assessment studies.

In such studies it is usually necessary to estimate mortality for exposures at a number of different combinations of concentration and time and in this case the lethal load function is usually expressed in the form

$$L^* = \Sigma C^n T \qquad [18.11.5]$$

where C is the concentration (ppm) and T is the time (min). The lethal load function in the form of Equation 18.11.5 has been widely used in hazard assessment.

For the case where $n = 1$ so that the load becomes $L = ct$, it is possible to define the LCt value. In particular, use is made of the LCt_{50}.

The relation between toxic load and mortality is usually a log–normal distribution and may therefore be plotted on log–probability paper. It may also be expressed as a probit equation

$$Y = k_1 + k_2 \ln L^* \qquad [18.11.6]$$

where Y is the probit and k_1, k_2 are constants.

It is a matter of indifference which expression, Equation 18.11.3 or Equation 18.11.4, is used to define the toxic load which causes a specified degree of injury; both give the same numerical results. In principle, it would be possible to distinguish between the two forms if one fitted better than the other the load–mortality distribution generally used, but in fact the distribution almost universally used for intensity–injury relationships in hazard assessment, not just for toxic gases but also for fire and explosion, is the log-normal distribution. With this distribution, if L is log-normally distributed, so is L^*.

Similarly, in the corresponding probit equation use of L^* instead of L is equivalent to multiplying the constant k_2 by m. Thus it is not possible to distinguish between the two forms.

There are, however, other arguments. From the point of view of hazard assessment, in which it is usually necessary to integrate the lethal load function, the definition of load given in Equation 18.11.4, or its discrete form Equation 18.11.5, is the more convenient.

There are also arguments, however, for the alternative form. Here toxicokinetic models appear relevant. For example, a one-compartment model for the body fluid concentration of the toxin with first-order excretion and constant gas concentration is equivalent to a first-order exponential stage with a step input, which gives a concentration rise of the form $[1 - \exp(-kt)]$, where k is a constant. It may be significant that this exponential rise may be approximated by a suitably scaled expression in $t^{\frac{1}{2}}$.

18.12 Gas Toxicity: Experimental Determination

The main source of information on the lethal toxicity of gases is experimentation on animals, particularly mice. In a typical study, groups of mice are exposed to different concentrations of gas for a single exposure period and the mortality is determined over a given period of observation after the exposure is over.

For a particular gas, assuming there are any data, there will typically be between one and half a dozen studies quoted in the literature which appear applicable. There may be one or two in which the exposure period has been varied. There may also be one or two studies with other species such as rats, guinea-pigs, rabbits, and, in older work mainly, cats and dogs.

The determination of the lethality of a toxic gas by inhalation experiments with animals is a difficult undertaking and is subject to various sources of error. In addition to the concentration of the gas and the exposure time, other important variables are the caging conditions, the breed, sex, age and health of the animals, and their behaviour, including their breathing rate. The animals may not die immediately and it is necessary to observe delayed deaths over a period of time, usually 10 days, and to record both immediate and delayed deaths. A sufficient number of animals needs to be used to obtain results with a high level of confidence, and pathological examinations should be conducted. The toxicity data sought are usually for a given exposure time and comprise the LC_{50} together with suitable values nearer the extremes of mortality such as the LC_{10} and LC_{90}.

18.12.1 Statistical interpretation of experiments

The statistical interpretation of experiments in toxicology was discussed in Section 18.3.

The method of Litchfield and Wilcoxon (1949) is convenient for the statistical treatment of results on inhalation toxicology. The application of this method to concentration mortality data for dogs exposed to chlorine is given in Section 18.18.

The lethal toxicity estimates required for hazard assessment are essentially the LC_{50}, the slope of the concentration mortality line, which may be expressed in terms of the ratio LC_{90}/LC_{10}, and the toxic load function, which defines the equivalence between concentration and time.

18.12.2 Estimation of lethal toxicity to animals

Usually, if there are any data at all, there will be enough to permit some estimate to be made not only of the LC_{50} but also of the ratio LC_{90}/LC_{10}, but the latter estimate will generally be such as to yield much less confidence in the LC_{10} than in the LC_{50}.

For some gases there may be a single set of experiments on one species, for others several sets on one species and for others again several sets on different species.

In the first case the estimate is straightforward, but where there are several sets of experiments on one species, there may be appreciable differences, say a factor of 2, in the LC_{50} reported by different authors, even though each group of workers reports relatively narrow confidence limits for its results.

In the second case where there are differences in the LC_{50} reported, it is necessary to decide whether to average the results or to select those which appear of highest quality. Each case must be treated on its merits.

The third case, where different species are involved, is discussed below.

In general, the lethal toxicity is a function of concentration and time. Although concentration may sometimes be completely dominant, there tends to be a trade-off between the two, so that at a particular value of the toxic load there is a given degree of lethality.

The experimental data from which to determine the index m in Equation 18.6.3 or n in Equation 18.6.4 are often sparse and in weak agreement. Work by Doe and Milburn gives a value for n of about $\frac{1}{2}$ for many of the irritant gases but about 1 for some other gases.

18.12.3 Extrapolation between species

Extrapolation of results obtained on one particular species to another species is beset with many difficulties, but it is an unavoidable step in the estimation of toxicity. Some accounts of the principles were mentioned in Section 18.3. In relation to inhalation toxicity specifically, reference may also be made to the accounts given by Flury and Zernik (1931) and Wachtel (1941), who worked on the toxicity of war gases, and to the Major Hazards Assessment Panel (MHAP) monographs (MHAP, 1987, 1988, 1993) described below.

The crucial question is whether or not the toxic effects are the same, or at least sufficiently similar, in the two species, thus providing a basis for extrapolation. Other important features are the relative modes and rates of inhalation and the mechanisms and rate of elimination, or metabolism.

In the case of irritant gases the toxic effects in the main laboratory animals and in man appear to be broadly similar, in that gas attacks the respiratory system. The fact that for these gases it is, the respiratory system which is the target means that metabolism is not significant. It is necessary to consider, however, the locus of action for each gas in each species, bearing in mind the solubility of the gas and the anatomy and respiratory behaviour.

Table 18.14 *Some principal physiological parameters of animals, including humans, relevant to respiration (Withers and Lees, 1986a) (Courtesy of the Institution of Chemical Engineers)*

A Animals, including man (after Altman and Dittmer, 1974)

	Species				
	Mouse	*Rat*	*Rabbit*	*Dog*	*Man*
Body weight (kg)	0.023	0.14	3.6	22.8	75.0
Lung volume (ml)	0.74	6.3	79	1501	7000
Alveolar surface area (m^2)	0.068	0.39	5.9	90	82
Minute volume (at rest) (ml/min)	24	84	1042	2923	6000
Minute volume/body weight (ml/min kg)	1043.5	600	289.4	128.2	80
Minute volume/lung volume (ml/min ml)	32.4	13.3	13.2	1.95	0.86
Minute volume/alveolar surface area ($ml/min\ m^2$)	352.9	215.4	176.6	32.5	73.2
Lung volume/alveolar surface area (ml/m^2)	10.9	16.2	13.4	16.7	85.4

B Man (after Mountcastle, 1974)

		Reference[a]
Body weight (kg)	75	1009
Lung volume (ml)	6000	1367
Tidal volume (ml)	500	1382
Alveolar volume (ml)	350	J.B. West (1965)
Anatomical dead space (ml)	150	J.B. West (1965)
Breathing rate (at rest) (breaths/min)	12	1382
Minute volume (at rest) (ml/min)	6000	1382
Alveolar surface area (m^2)	70	1387
Pulmonary diffusion capacity for carbon monoxide, D_{LCO} (ml/min mm Hg)	61	1391
Mean thickness of alveolar capillary tissue barrier (μm)	1.7	Altman and Dittmar (1974)
Volume of lung capillaries (ml)	140	1387
Residence time of blood in lung capillaries (s)	0.75	1387
Volume of blood (ml)	5000	844
Volume of plasma (ml/kg body weight)	45	1020
Volume of cell fluid (ml/kg body weight)	30	1020

[a] Page number in Mountcastle (1974), unless otherwise noted.

18.12.4 Animal physiology

In many cases extrapolation from animals to humans is supported by an argument based on the ratio of physiological quantities such as the minute volume or body weight.

Information on animal physiology is given in *The Rat – Data and Reference Tables for the Albino Rat* (Donaldson, 1924), *The Rat in Laboratory Investigation* (Farris and Griffiths, 1949), *Handbook of Biological Data* (Spector, 1956a), *Blood and Other Body Fluids* (Altman and Dittmer, 1961), *Metabolism* (Altman and Dittmer, 1968), *Respiration and Circulation* (Altman and Dittmer, 1971), *Biology Data Book* (Altman and Dittmar, 1974), *Clinical, Biochemical and Hematological Reference Values in Normal Experimental Animals* (Mitruka and Rawnsley, 1977) and *Inbred and Genetically Defined Strains of Laboratory Animals. Part 1, Mouse and Rat* (Altman and Katz, 1979).

Data on some of the principal parameters of animal physiology relevant here are given in Table 18.14.

18.12.5 Vulnerable populations

Extrapolation from animals to man is usually done in the first instance for healthy young adults. It may be necessary, however, to allow for vulnerable members of the population.

It is commonly assumed in hazard assessment that a section of the population, including young children and old people, is particularly vulnerable. In the case of toxic gas hazard, those with respiratory disease are also included. However, this is an aspect on which very little work has been done.

It may be preferable to derive separate estimates of the lethal toxicity for the regular and vulnerable populations. This makes it possible to allow for differences

in the numbers and composition of the exposed population at different times of day.

18.13 Gas Toxicity: Physiological Factors

18.13.1 Respiration

Any attempt to model the toxic effects of inhaled gases requires some understanding of the respiratory process.

Accounts of the respiratory system, the effects of gases on this system and the absorption of gases into the blood include those given in: standard texts on general physiology, such as *Handbook of Physiology* (Fenn and Rahn, 1964), *Medical Physiology* (Mountcastle, 1974) and *Samson Wrights Applied Physiology* (Keele, Neil and Joels, 1982); texts on the respiratory system, such as *The Morphometry of the Human Lung* (Weibel, 1963), *Ventilation Blood Flow and Gas Exchange* (J.B. West, 1965), *Human Respiration* (Lippold, 1968), *Physiology of Respiration* (Comroe, 1974), *Lung Function* (Cotes, 1979), *Lung Connective Tissue* (Pickrell, 1981), *Modelling and Control of Breathing* (Whipp and Wiburg, 1983), *Inhalation Studies* (Phalen, 1984) and MS 5 *Lung Function* (HSE, 1977); and in texts on the inhalation of gases, such as *Modeling of Inhalation Exposure to Vapor* (Fiserova-Bergerova, 1983).

The account given here describes in outline the respiratory process and some of the quantitative data and relations in respiratory physiology. This information is the starting point for modelling the effect of toxic gases, both irritant gases which attack the lungs and other gases which enter the blood. The data given are taken mainly from Mountcastle (1974) and apply to a young adult male, unless otherwise stated.

The respiratory system is illustrated in Figure 18.4. Air entering the lung passes through the trachea, then down the bronchioles and through the alveolar duct into the alveolar sac. Interchange between the air and the blood occurs at the surface of the alveoli.

The walls of the capillaries lining the alveoli are extremely thin. The equilibrium partial pressure of a solute gas in the alveoli is effectively the same as that above the blood, neglecting the membrane. Mass transfer between the air and the blood is very rapid.

The volume of air moved in one respiratory cycle is less than the total capacity of the lungs. Moreover, not all the air moved enters the alveolar space, since there is dead space. It is necessary, therefore, to define a number of components of lung volume as shown in Figure 18.5. These include:

Tidal volume (TV)	Volume of air entering and leaving the lungs in one natural respiratory cycle.
Inspiratory reserve volume (IRV)	Volume of air additional to the tidal volume which can be inhaled by maximum effort.
Expiratory reserve volume (ERV)	Volume of air additional to tidal volume which can be exhaled by maximum effort.
Residual volume (RV)	Volume of air remaining in lungs after exhalation with maximum effort

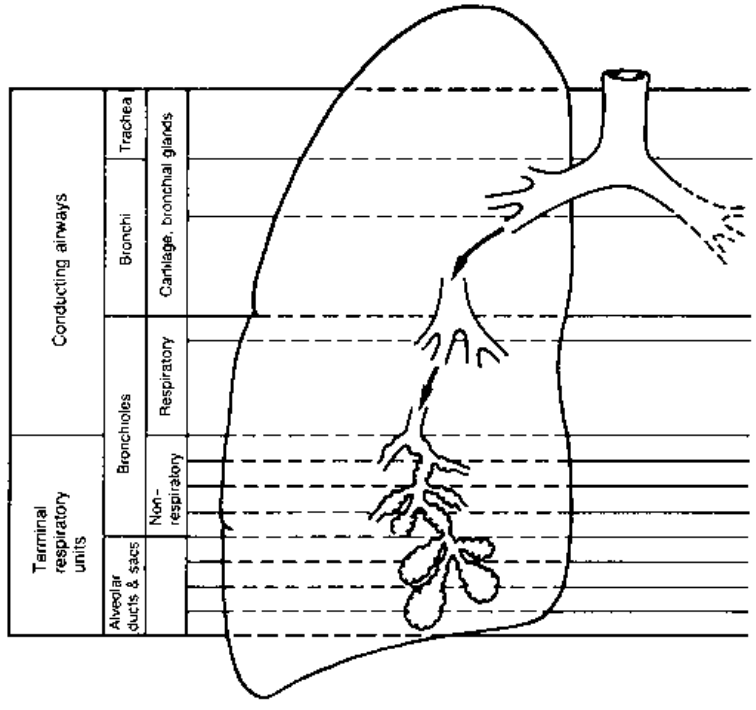

Figure 18.4 *The structure of the respiratory tree in the lung (after Weibel, 1973)*

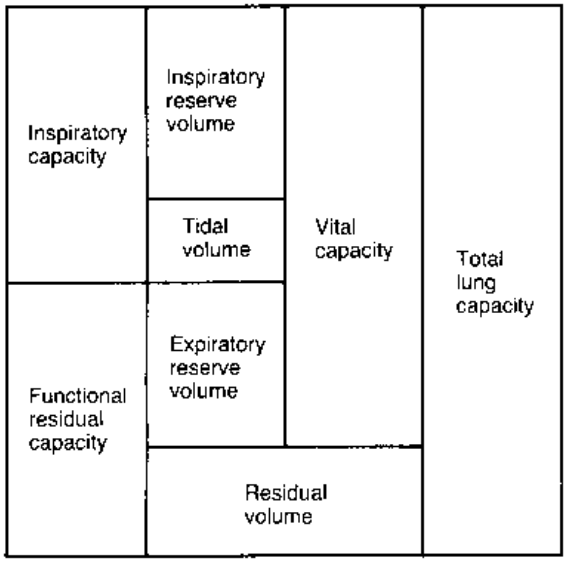

Figure 18.5 *Components of lung volume (after Lambertsen, 1974; Cotes, 1979)*

Vital capacity (VC)	Sum of tidal, inspiratory reserve and expiratory reserve volumes.
Inspiratory capacity (IC)	Volume of air which can be inhaled with maximum effort; sum of tidal volume and inspiratory reserve volume
Functional residual volume (FRV)	Volume of air left in lungs at end of natural exhalation
Total lung capacity (TLC)	Sum of vital capacity and residual volume. Also sum of inspiratory capacity and functional residual capacity

Thus

$$\begin{aligned}TLC &= VC + RV = IRV + TV + ERV + RV \\ &= IC + FRC\end{aligned}$$
$$VC = IRV + TV + ERV$$
$$IC = IRC + TV$$
$$FRC = ERV + RV$$

The tidal volume consists of the alveolar space and the anatomical dead space. Some typical values are:

Tidal volume, $V_T = 500$ ml
Alveolar space, $V_A = 350$ ml
Anatomical dead space, $V_D = 150$ ml

The typical respiration rate at rest is

Respiration rate, $f = 12$ breaths/min

The product of the tidal volume and the respiration rate is termed the minute volume, $\dot{V}_T$ and that of the alveolar space and the respiration rate the alveolar ventilation, $\dot{V}_A$. Typical values of these two quantities are

Minute volume, $\dot{V}_T = 12 \times 500 = 6000$ ml/min
Alveolar ventilation, $\dot{V}_A = 12 \times 350 = 4200$ ml/min

The lungs contain some 3×10^8 alveoli with an alveolar area of about $70\,m^2$. The thickness of the capillary membrane is about 0.3–2.5 μm. The capillary volume is some 140 ml and the transit time of the blood is some 0.75 s at rest and 0.34 s during exercise.

The flow of blood through the capillaries of the lung depends on the cardiac output, which is a function of the heart rate and the stroke volume. The heart rate is typically 75 strokes/min and the stroke volume some 77 ml, and the cardiac output about 5000 ml/min.

It is the function of the lung to absorb oxygen from the air into the blood and to desorb carbon dioxide from the blood into the air. The measure of the ability of the lung to do this is pulmonary diffusion capacity D_L. The pulmonary diffusion capacity for oxygen is defined by the relation

$$D_{LO2} = \frac{\dot{V}_{O2}}{P_{AO2} - P_{AO2'}} \qquad [18.13.1]$$

where D_{LO2} is the pulmonary diffusion capacity for oxygen (ml/min mm Hg), P_{AO2} is the partial pressure of oxygen in the alveolar space (mmHg), $P_{AO2'}$ is the equilibrium partial pressure of oxygen in the alveolar space and above the pulmonary capillaries (mm Hg) and $\dot{V}_{O2}$ the rate of absorption of oxygen (ml/min). The diffusion capacity for carbon dioxide D_{LCO2} is defined in a similar way.

In practice, the principal measured values relate to the diffusion capacity of carbon monoxide D_{LCO}. Carbon monoxide has a very high affinity for haemoglobin, some 210 times that of oxygen, so that the equilibrium partial pressure of carbon monoxide in the alveolar space is very small and may be neglected in estimating the diffusion coefficient.

The diffusion capacity of a gas is proportional to its solubility and inversely proportional to the square root of its molecular weight. The solubilities of oxygen and carbon dioxide at 37°C are for water 2.386 and 56.7 ml gas/100 ml fluid atm and for plasma 2.14 and 51.5 ml gas/100 ml fluid atm, respectively. The diffusion capacity for oxygen D_{LO2} is $1.23 \times D_{LCO}$ and that for carbon dioxide is $24.6 \times D_{LCO}$. The ratio D_{LCO2}/D_{LO2} is 20.

The value of D_{LO2} at rest is about 75 ml/min mm Hg.

Partial pressures of oxygen in respiration are: approximately:

	Partial pressure of oxygen (mm Hg)
Ambient air	158
Tracheal air	149
Alveolar air	100
Exhaled air	116

The partial pressure of the exhaled air is the weighted average of the tracheal and alveolar air. The equilibrium partial pressure of oxygen above arterial blood $P_{O2a'}$ is

about 95 mm Hg and that above venous blood $P_{O2v'}$ about 40 mm Hg.

Blood comprises plasma and cells. The volume of plasma is some 45 ml/kg body weight and that of cells some 30 ml/kg body weight. For a man of 70 kg the volume of plasma is therefore about 3150 ml and that of blood about 5250 ml.

Extracellular fluid comprises some 20% and plasma some 5% of body weight. Thus extracellular fluid other than plasma has a volume some 3 times that of the plasma. All but a very small fraction of this extracellular fluid is in diffusion equilibrium. The specific gravity of plasma is 1.026.

Some principal relations for lung volumes, ventilation rates and partial pressures are

$$V_T = V_E = V_A + V_D \quad [18.13.2]$$

$$\dot{V}_A = V_A f \quad [18.13.3]$$

$$\dot{V}_E = V_E f \quad [18.13.4]$$

$$\dot{V}_I = \frac{F_{EN2}}{F_{IN2}} \dot{V}_E \quad [18.13.5]$$

$$\dot{V}_{O2} = \dot{V}_I F_{IO2} - \dot{V}_E F_{EO2} \quad [18.13.6]$$

$$F_{EO2} = (F_{IO2} V_D + F_{AO2} V_A)/V_E \quad [18.13.7]$$

$$\dot{V}_{O2} = D_{LO2}(P_{AO2} - P_{AO2'}) \quad [18.13.8]$$

$$P_{AO2'} \approx P_{O2a'} \quad [18.13.9]$$

$$P_{O2'} = C_{O2}/H_{O2} \quad [18.13.10]$$

where C_{O2} is the concentration of oxygen in the liquid phase (ml O_2/ml fluid), D_{LO2} is the pulmonary diffusion capacity for oxygen (ml/min mm Hg), F_{AO2} is the concentration of oxygen in alveolar space (ml O_2/ml space), F_{EN2} is the concentration of nitrogen in the exhaled air (ml N_2/ml air), F_{EO2} is the concentration of oxygen in the exhaled air (ml O_2/ml air), F_{IN2} is the concentration of nitrogen in the exhaled air (ml N_2/ml air), F_{IO2} is the concentration of oxygen in the inhaled air (ml O_2/ml air), H_{O2} is Henry's law constant for oxygen (ml O_2/ml fluid (mmHg O_2)), P_{AO2} is the partial pressure of oxygen in the alveolar space (mmHg), $P_{AO2'}$ is the equilibrium partial pressure of oxygen at the capillary membrane (mmHg), $P_{O2'}$ is the equilibrium partial pressure of oxygen (mmHg), $P_{O2a'}$ is the partial pressure of oxygen above arterial blood (mmHg), V_A is the alveolar volume (ml), $\dot{V}_A$ is the alveolar minute volume (ml/min), V_D is the anatomical dead space (ml), V_E is the volume exhaled (ml), $\dot{V}_E$ is the exhaled minute volume (ml/min), $\dot{V}_I$ is the inhaled minute volume (ml/min), $\dot{V}_{O2}$ is the oxygen consumption minute volume (ml/min), V_T is the tidal volume (ml), and f is the respiration rate (breaths/min).

Some principal physiological parameters in man relevant to respiration have been given in Table 18.14. Further data on the lung in man are summarized in Table 18.15.

Table 18.15 *Some principal parameters of the lung in man (after Mountcastle, 1974) (Courtesy of CV Mosby Company)*

A Lung volumes

	Volume (ml)
Total lung capacity	5970
Tidal volume	500
Expiratory reserve volume	980
Residual volume	1190
Vital capacity	4780
Inspiratory capacity	3790
Functional residual volume	2180
Anatomical dead space	150[a]
Alveolar volume	350[a]

[a] J.B. West (1965).

B Respiration rate

	Rate (breaths/min)
At rest	12

18.13.2 Toxicokinetic models

The treatment just given of the respiratory system provides the front-end part for a toxicokinetic model describing the absorption and distribution of the toxin in the body.

Such toxicokinetic models for an inhaled gas may be developed by modelling the absorption of gas in the lung into the bloodstream. The difference between the mass inhaled and that exhaled equals the mass transferred across the membrane of the lung and this in turn equals the mass deposed in the body. Then if the chemical enters the main bloodstream, its concentration in the blood will be a function of the rates of absorption and of elimination. In simple terms, this situation may be modelled as a single exponential stage with a time constant which is a function of the apparent volume of distribution. The equilibrium back pressure of the chemical at the lung surface will depend on the concentration in the blood.

A toxicokinetic model of this general type is applicable where the toxic gas does not attack the respiratory system, but enters into the bloodstream and attacks some other organ in the body. There is, however, a lack of models relevant to hazard assessment.

18.13.3 Irritant gases

Such models are, in any case, less applicable to the important class of irritant gases, which act directly on the surface of the respiratory tract and/or lung rather than by accumulation in the body fluids. In this case the respiratory system acts as a sink for the chemical. This clearly requires a different model but, again, models suitable for hazard assessment are lacking.

18.13.4 Inhalation rates

In most cases the inhalation rate is a dominant factor in the entry of toxic gas into the system. It is therefore of

Table 18.16 *Inhalation rate for various levels of activity for man (after Henderson and Haggard, 1943)*

Activity	*Inhalation rate*[a] (l/min)	*Oxygen consumption rate*[b] (l/min)
Rest in bed, fasting	6	0.240
Sitting	7	0.300
Standing	8[c]	0.360
Walking, 2 mile/h	14	0.650
Walking, 4 mile/h	26	1.200
Slow run	43	2.000
Maximum exertion	65–100	3.000–4.000

[a] Measured at 0°C and 760 mm Hg.
[b] Measured at 20°C.
[c] This value is quoted by A. Meyer (1938) and also by Prentiss (1937).

great importance both in modelling the effects of and in extrapolating from experiments on toxic gases.

In applying to man the results of animal experiments on gas toxicity it is necessary to make allowance for the effect the of inhalation rate. If the base case for comparison between animals and man is that each has the inhalation rate which is normal at rest, there are two separate allowances, or factors, which need to be applied. The first is between the inhalation rate of the animal at rest and in the experiment, the second between that of man at rest and in the accident conditions envisaged in the hazard assessment. It can be seen from Table 18.14 that there are appreciable differences in the inhalation rates, as related to features such as body weight and lung surface area.

Information on the breathing of animals during exposure is recorded in some experiments, although quantitative data appear to be relatively rare. By contrast, the variation of the inhalation rate of man with different degrees of exercise is well documented. Some data given by Henderson and Haggard (1943) are shown in Table 18.16.

18.13.5 Other factors

The respiratory system is not the only organ which is a target for toxic gases. The eyes and the skin may also be affected. Accounts of the eye relevant here are given in *Toxicology of the Eye* (Grant, 1962) and *Synopsis of Ophthalmology* (Havener, 1971).

18.14 Gas Toxicity: Toxicity Data

Before considering the toxicity of some of the principal industrial gases, attention is drawn to some of the general sources of data on toxicity, particularly toxicity to humans.

Sources of toxicity data have been described in Section 18.3. Some texts which deal particularly with gas toxicity include: *Kompendium der praktischen Toxikologie* (Kobert, 1912); *Industrial Poisoning* (Rambousek, 1913); *Kurzes Lehrbuch der Arbeits- und Gewerbehygiene* (Lehmann, 1919); *Industrial Poisons in the United States* (Hamilton, 1925); *Lehrbuch der Toxikologie* (Flury and Zanger, 1928), *Noxious Gases* (Henderson and Haggard, 1943); *Industrial Hygiene and Toxicology* (Patty, 1948–), with its later editions (Cralley and Cralley, 1978; Wands, 1981; Clayton and Clayton, 1991 ACGIH/73); *Dangerous Properties of Industrial Materials (Sax*, 1957–), with its later edition (Lewis, 1992 ACGIH/89); *Toxicology of Drugs and Chemicals* (Deichman and Gerarde, 1969); and *Toxicology: the Basic Science of Poisons* (Casarett and Doull (1975), with its later edition (Amdur, Doull and Klaassen, 1991 ACGIH/54).

At the turn of the century an appreciable amount of research was done in Germany by Lehmann and others on the effects on humans of many gases of industrial interest. This includes work by Lehmann himself (Lehmann, 1886, 1887, 1893, 1899a) and by Matt (1889); there is also later work by Hess (1911), Drescher (1920) Dschang (1928) and Beck (1959).

Many of the main industrial gases have also been used in warfare, particularly in the First World War. Accounts of the military use of these gases do not generally provide usable quantitative data, but some give pointers to the effects of the gases on humans which constitute a collateral check on data from animal experiments, which is the main source.

Accounts of the gas warfare are given in *The Poison War* (A.A. Roberts, 1915), *Reports* of the Chemical Warfare Medical Committee (1918–), *Atlas of Gas Poisoning* (MRC, 1918), *The Lethal War Gases* (Underhill, 1920), *Chemical Warfare* (Fries and West, 1921), *History of the Great War, Medical Services, Diseases of the War,* vol. II (Macpherson *et al.*, 1923), *Gas Warfare* (Fischmann, 1924), *Poisoning Warfare Gases* (Gilchrist, 1924), *Fünf Vortrage aus den Jahren 1920–1923* (F. Haber, 1924), *La Guerre Chimique* (Le Wita, 1925), *The Medical Aspects of Chemical Warfare* (Vedder, 1925), *The Medical Department of the United States Army in the World War,* vol. 14: *Medical Aspects of Gas Warfare* (Ireland, 1926), *Der Gaskampf und die chemischen Kampfstoffen* (J. Meyer, 1926), *History of the War: Military Operations in France and Belgium* (Edmonds and Wynne, 1927), *A Comparative Study of World War Casualties from Gas and Other Weapons* (Gilchrist, 1928), *Manual of Treatment of Gas Casualties* (Anon., 1930), *Schadliche Gase* (Flury and Zernik, 1931), *Grün und Gelbkreuz* (Buscher, 1932), *(Die wichtigsten Vergiftungen Die Gasschutzfrage* (Zangger, 1932), Loschke, 1933), *Gas. The Story of the Special Brigade* (Foulkes, 1934), *Leitfaden der Pathologie und Therapie der Kampfgaserkrankungen* (Muntsch, 1935), *Die Tiere im chemischen Krieg* (Richters, 1936b), *Der chemische Kreig* (Hanslian, 1937), *Chemicals in War* (Prentiss, 1937), *Breathe Freely* (Kendall, 1938), *Gaz de Combat* (A. Meyer, 1938), *The War Gases* (Sartori, 1939), *Chemical Warfare* (Wachtel, 1941), *United States Army in World War II: The Technical Services: Chemical Warfare Service* (Brophy, Miles and Cochrane, 1959), *The Problem of Chemical and Biological Warfare,* vol. 1: *The Rise of CB Weapons* (J.P. Robinson, 1971) and *The Poisonous Cloud. Chemical Warfare in the First World War* (L.F. Haber, 1986). Other work on war gases is described by L. Hill (1915, 1920), Haldane, Meakins and Priestley (1918a,b, 1918/19), Herringham (1919, 1920), Flury (1921a,b), Haggard (1924), Chlopin (1927–) and Richters (1936b).

Accounts of thephysiological and medical aspects of gas poisoning are given in *Respiratory Function of the*

Blood (Barcroft, 1925), *Respiration* (Haldane and Priestley, 1935), *and Pulmonary Oedema and Inflammation* (Drinker, 1945).

Some authors have dealt in a single publication with a number of different gases. They include Lehmann (1893, 1899a), Ronzani (1908, 1909), Hess (1911), Zeehuisen (1922), Haggard (1924), Schutze (1927), Walton and Witherspoon (1928), Carpenter, Smyth and Pozzani (1949), Smyth and Carpenter (1949), Zielhuis (1970), Higgins *et al.* (1972), MacEwen and Vernot (1972), Vernot *et al.* (1977) and ten Berge, Zwart and Appelman (1986).

Setterstrom and co-workers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940) have studied ammonia, chlorine, hydrogen cyanide, hydrogen sulphide and sulphur dioxide.

A somewhat separate area of work which also yields toxicity data is that on the toxicity of combustion products. Accounts of research in this area, notably by Hilado and co-workers and by Hartzell and co-workers, are given in Section 18.22.

An early collection of gas toxicity data for hazard assessment is that given in the Vulnerability model of Eisenberg, Lynch and Breeding (1975), and extended by Perry and Articola (1980). Their work is discussed below. Another collection of data on gas toxicity is that made by Back, Thomas and MacEwen (1972).

18.15 Gas Toxicity: Vulnerability Model

18.15.1 Initial model

As just stated, some of the first correlations for the toxicity of industrial gases relevant to major releases were those given in the vulnerability model by Eisenberg, Lynch and Breeding (1975). These workers analysed data for the toxicity of chlorine and ammonia and obtained probit equations for the lethality of these two gases. For chlorine they found that the line for composite lethality in animals passes through the following points:

Arbitrary units	*Percent affected*
0.54	3
0.59	5
1	50
1.5	90
1.8	97 (extrapolated)

They also refer to the *Guide for Short-Term Exposure* for chlorine (NAS/NRC, 1973), which describes an exposure of 14–21 ppm for $\frac{1}{2}$–1 hours as 'dangerous' and one of 34–51 ppm for 1–1$\frac{1}{2}$ hours as 'lethal'. They suggest that the terms 'dangerous' and 'lethal' might be interpreted as 5% and 90% lethal.

Eisenberg, Lynch and Breeding quote limit values given in the *Guides* for chlorine (NAS/NRC, 1973) and ammonia (NAS/NRC, 1972b). At the short term exposure limit (STPL), there is mild odour, minimal irritation and no health hazard. The STPL values for chlorine and ammonia are:

Time (min)	*Concentration* (ppm)	
	Chlorine	*Ammonia*
10	1	20
30	0.5	10
60	0.5	10

At the public emergency limit (PEL), there is strong odour and some irritation. The PEL values, which are ceilings, not averages, for chlorine and ammonia are:

Time (min)	*Concentration* (ppm)	
	Chlorine	*Ammonia*
10	3	100
30	2	75
60	2	50

In addition, they quote for chlorine the emergency exposure limit (EEL) suggested by Zielhuis (1970):

Time (min)	*Concentration* (ppm)
5	7
15	5
30	4
60	3

On the basis of such arguments the authors give for chlorine the following response relations:

Chlorine concentration (ppm)	*Time of exposure*	*Effect*
3	Any	No risk, but some harassment
7	1 h or more	Strong to intolerable irritation, with some risk to highly susceptible individuals
20	Several hours	50% lethal (their estimate)
33	c. 1 h	50% lethal (estimate based on NAS/NRC report)
60	c. 10 min	50% lethal (their estimate)

Eisenberg, Lynch and Breeding took the causative factor V in the probit equation for chlorine as

$$V = \Sigma C_i^n T_i \qquad [18.15.1]$$

where C is the concentration (ppm), T is the time interval (min), and n is an index. From analysis of the data, they obtained a value of $n = 2.75$. The probit equation for chlorine lethality derived by these authors is then

$$Y = -17.1 + 1.69 \ln(\Sigma C_i^{2.75} T_i) \quad [18.15.2]$$

where Y is the probit.

A similar treatment was applied to ammonia. For this gas the authors give the following response relations:

Ammnonia concentration (ppm)	*Time of exposure*	*Effect*
20	Any	Odour detected by majority of population
100	Any	Irritation and complaint
500	Any	Strong to interolable irritation, with some risk to highly susceptible individuals
2500–5000		Fatalities mostly from a few in the first 5 min to 90–100% after 1 h, depending on concentration
>5000		100% fatal. Heavy casualties in 5–10 min, and shorter exposures are unlikely in practice

and derive the following probit equation for ammonia lethality:

$$Y = -30.57 + 1.385 \ln(\Sigma C_i^{2.75} T_i) \quad [18.15.3]$$

The relationships described apply to healthy adults. The population also includes more susceptible individuals such as infants, old people and people with advanced pulmonary/cardiovascular disease. The authors propose for such high risk populations the scaling shown in Table 18.17, which is applied to specific concentrations and exposure times for chlorine and ammonia.

Eisenberg, Lynch and Breeding also consider non-lethal injury from chlorine. They give the following estimated response:

Chlorine concentration (ppm)	*Percent affected*
6	1
10	25
13	50
20	90

In this case the causative factor is taken simply as $V = C$. The probit equation for non-lethal injury from chlorine is then

$$Y = -2.40 + 2.90 \ln C \quad [18.15.4]$$

Non-lethal injury is here taken to mean hospitalization without or with lasting impairment of health.

Table 18.17 *Relation between the lethal concentration of chlorine for the general population and a vulnerable population (Eisenberg, Lynch and Breeding, 1975)*

Level of effect	*Deaths (%)*	
	General population	*High risk population*
Severe harrassment with some risk	0	25
Lethal	3	50
Lethal	50	100

The authors discuss the possible long-terms effects of exposure to chlorine. They state:

> The most recent paper seen was Weill *et al.* (1969). They say that their data for subjects seven years after an accidental exposure to chlorine 'are consistent with the prevailing clinical view that significant permanent lung damage does not result from acute exposure to chlorine gas'. Reports referenced in their paper support this finding: for example, 'no evidence that chlorine intoxication produced residual pulmonary disease' in the 33 most severely affected victims of a major accident; a large survey of industrial exposures did not find 'any evidence of permanent damage to the respiratory tract' another study including war casualties found that 'permanent pulmonary injury was rare'.

18.15.2 Development of model

A further set of probit equations for lethality for use in the Vulnerability model was derived by Perry and Articola (1980). For chlorine the authors quote without reference a set of 'best estimates' which seem close to the data set given by Eisenberg, Lynch and Breeding (Table 6–4) but use a slightly different value of n (2.64 instead of 2.75). For ammonia, they refer again to the data set given in Eisenberg, Lynch and Breeding (Table 6–4). They use in this case an appreciably different value of n (1.36 instead of 2.75).

For hydrogen cyanide the authors use estimates made by McNamara (1976) based on animal data. They also adapt these data for two other gases, acrylonitrile and hydrogen sulphide, having found no suitable data for these substances. In the latter case they quote C.L. Evans (1967) on the similarities between the effects of the two gases. For acrylonitrile they use the same lethal dose values and probit equation as for hydrogen cyanide, whilst for hydrogen sulphide they double the lethal dose values compared with hydrogen cyanide and thus obtain a different probit equation.

For hydrogen fluoride they utilize data from an earlier study for the Vulnerability model by Rausch, Tsao and Rowley (1977) based on data from Braker and Mossman (1970), Darmer, Haun and MacEwen (1972), Higgins *et al.* (1972), MacEwen and Vernot (1974) and Wohlslagel, DiPasquale and Vernot (1976). They adopt the same value of n namely $n = 1$; in other words, Haber's law.

For hydrogen chloride, Perry and Articola utilize data from another previous study for the Vulnerability model, that by Rausch, Eisenberg and Lynch (1977). The value

of n is 1.0. They use same lethal dose values and value of n for sulphur dioxide (in mg/m^3), the difference in the probit equations being due to the conversion to ppm.

For phosgene, the authors again utilize data from Rausch, Eisenberg and Lynch. The value of n is 1.0.

Two probit equations for non-lethal injury are also given: that given by Eisenberg, Lynch and Breeding for chlorine and one derived by the authors themselves for hydrogen fluoride.

The values of the parameters in the probit equations obtained by Perry and Articola are given in Section 18.20.

The support for the probit equations in the Vulnerability model is in some cases rather slight and the level of physical activity to which they are applicable is not well defined.

18.16 Gas Toxicity: Major Industrial Gases

The toxicity of a number of major industrial gases is now considered in more detail. In general, toxic hazard from these gases arises from their manufacture, storage and use in the manufacture of other chemicals. In some cases, hazard arises from another cause. For example, a common cause of gassing by hydrogen sulphide is its presence as an impurity in crude oil and in confined spaces. The overview of the physiological effects of the main industrials gases given in *Noxious Gases* (Henderson and Haggard, 1943) provides a useful introduction to this aspect.

For irritant gases, an important parameter is the solubility in water, which largely determines the part of the respiratory system attacked. Haggard (1924) gives the following relative figures for the solubility of such gases in water at 40°C: ammonia, 444 (extrapolated); hydrogen chloride, 385; sulphur dioxide, 18.7; bromine, 9.4; and chlorine, 1.4. No value is given for phosgene, which decomposes in water.

Incidents involving toxic gases are described in Section 18.27.

18.16.1 Chlorine

There are two industrial toxic gases which in liquefied form are handled on a large scale and are readily dispersed and which therefore present a major toxic hazard. Chlorine is one, and ammonia the other.

Chlorine is a highly toxic gas. The long- and short-term OESs are 0.5 and 1 ppm, respectively. The values represent a small reduction from the TLV (TWA) of 1 ppm which held for many years. Physiologically, chlorine is an irritant gas. The effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema. A fuller account is given in Section 18.18.

Early work on chlorine includes that Eulenberg (1865), Lehmann (1887, 1899a,b) and Hess (1911). Chlorine was the first gas used in major gas attacks and is treated in virtually all the war gas texts referred to in Section 18.14, and in particular in Underhill (1920), Winternitz, Lambert *et al.* (1920), Gilchrist (1924), F. Haber (1924), Vedder (1925), Flury and Zernik (1931), Prentiss (1937), and by Black, Glenny and McNee (1915), Bradford and Elliott (1915–16), L. Hill (1915, 1920), Schafer (1915), Kramer (1917), Haldane, Meakins and Priestley (1918a,b, 1918–19), Schultz (1918a,b), Schultz and Hunt (1918), Achard (1919), Barbour (1919), Barbour and Williams (1919), Baskerville (1919), Burrell (1919), Herringham (1919, 1920), Hjort and Taylor (1919), Meakins and Priestley (1919), Vinet (1919), Gunn (1920), Flury (1921a, 1928), Chlopin (1927–), Flury and Zernik (1932), Abbott (1933), Gilchrist and Matz (1933) and Freitag (1940). More recent work includes that by Geiling and McLean (1941), Cralley (1942), Silver and McGrath (1942), Silver, McGrath and Ferguson (1942), Fowell (1949), A.T. Jones (1952), Elmes and Bell (1963), Gay (1963), Flake (1964), D.P. Bell and Elmes (1965), Kowitz *et al.* (1967), C.G. Kramer (1967), Rupp and Henschler (1967), Schlagbauer and Henschler (1967), Krause, Chester and Gillespe (1968), Beach, Jones and Scarrow (1969), Chester, Gillespie and Krause (1969), Sartorelli (1969), Faure *et al.* (1970), Sessa *et al.* (1970), Kaufman and Burkons (1971), Leube and Kreiter (1971), Barrow and Smith (1975), Colardyn *et al.* (1976), Barrow *et al.* (1977), Chester *et al.* (1977), Bitron and Aharonson (1978), Barrow and Dodd (1979), Barrow *et al.* (1979), Withers and Lees (1985a,b), Withers (1986a) and Zwart and Woutersen (1988). Work on chlorine is also included in treatments dealing with a number of gases, including those by Zeehuisen (1922), Haggard (1924), Setterstrom and co-workers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940), Carpenter, Smyth and Pozzani (1949), Beck (1959), and Buckley *et al.* (1984).

The toxicity of chlorine has been reviewed in *Chlorine and Hydrogen Chloride* by the (WHO, 1982 EHC21) and in the *Chlorine Toxicity Monograph* (MHAP, 1987); an account from the latter work has been given by Withers (1985). The *Monograph* estimates that in the absence of any subsequent medical treatment the LC_{50} for 30 minutes for healthy adults is of the order 400 ppm.

Probit equations for chlorine have been given by Eisenberg, Lynch and Breeding (1975), Perry and Articola (1980) ten Berge and van Heemst (1983), Withers and Lees (1985b), and ten Berge, Zwart and Appelman (1986), in the *Rijnmond Report* (Rijnmond Public Authority, 1982), and by the Center for Chemical Process Safety (CCPS) and the CPD. Dangerous dose values are given by the HSE, as described below.

Chlorine is one of the gases considered in the hazard assessment study of Back, Thomas and MacEwen (1972). The evidence is that serious long-term effects of non-lethal single exposure to chlorine are rare. This aspect is discussed in Section 18.15.

A fuller treatment of chlorine toxicity is given in Section 18.18.

18.16.2 Ammonia

The other principal industrial toxic gas is ammonia. Like chlorine, it is a severe toxic hazard because it is handled on a large scale, it is a liquefied gas and is therefore readily dispersed, and it is highly toxic. Ammonia has long- and short-term OESs of 25 and 35 ppm, respectively.

Physiologically, ammonia is an irritant gas. The effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema. Ammonia is very much more soluble in water than chlorine, and therefore tends to attack particularly

the upper respiratory tract, stripping the lining, and inducing laryngeal oedema.

Early work on ammonia includes that by Lehmann (1886, 1893), Matt (1889), Hess (1911) and Ronzani (1908, 1909). Ammonia does not appear to have been a candidate war gas, but it is discussed by Flury (1921a, 1928), Flury and Zernik (1931) and Henderson and Haggard (1943). More recent work includes that by Boyd, MacLachlan and Perry (1944), Silver and McGrath (1948), Silverman, Whittenberger and Muller (1949), Alpotov and Michailov (1963), H.A. Mitchell (1963), Alpotov (1964), Helmers, Top and Knapp (1971), Mayan and Merilan (1972), Hilado, Casey and Furst (1977), Verberk (1977), Richard, Jounay and Boudene (1978), Dodd and Gross (1980), Appelman, ten Berge and Reuzel (1982), Kapeghian *et al.* (1982), ten Berge and van Heemst (1983), Withers (1986b) and Pedersen and Selig (1989). Work on ammonia is also included in treatments dealing with a number of gases, including those by Haggard (1924), Setterstrom and co-workers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940), Carpenter, Smyth and Pozzani (1949), Coon *et al.* (1970), Stupfel *et al.* (1971), Vernot *et al.* (1977) and Buckley *et al.* (1984).

The toxicity of ammonia in the specific context of process plants has been considered by D.P. Wallace (1979).

The toxicity of ammonia has been reviewed in *Ammonia* (WHO, 1986 EHC54) and in *Ammonia Toxicity Monograph* (MHAP, 1988).

Probit equations for ammonia have been given by Eisenberg, Lynch and Breeding (1975), Perry and Articola (1980), ten Berge, Zwart and Appelmann (1986), the CCPS and the CPD. Dangerous dose values are given by the HSE, as described below.

Ammonia is one of the gases considered in the hazard assessment study done by Back, Thomas and MacEwen (1972).

There is little evidence of serious long-term effects of non-lethal single exposure, except where the exposure has been so serious that death has been prevented only by medical attention, when respiratory deficiencies may occur.

18.16.3 Acrylonitrile

Acrylonitrile is an irritant gas and is also assigned the 'risk phrase' R45. It has a long-term MEL of 2 ppm, but no quoted short-term limit.

Physiologically, acrylonitrile vapour causes various irritant effects including pulmonary oedema. Various other effects such as vomiting, convulsions and incoordination have been reported in animals.

Most work on the toxicity of acrylonitrile has been carried out since 1940. Studies include those of Dudley and Neal (1942), Dudley, Sweeney and Miller (1942), R.H. Wilson (1944), R.H. Wilson, Hough and McCormick (1948), Carpenter, Smyth and Pozzani (1949), McOmie (1949), Smyth and Carpenter (1949), Brieger, Rieders and Hoders (1952), Knobloch *et al.* (1971), Rogaczewska (1975), McNamara (1976), Appel, Peter and Bolt (1981) and ten Berge, Zwart and Appelman (1986).

Probit equations for acrylonitrile have been given by Perry and Articola (1980), ten Berge, Zwart and Appelman (1986), the CCPS and the CPD. Dangerous dose values are given by the HSE, as described below.

18.16.4 Bromine

Bromine is a highly toxic gas. It has long- and short-term OESs of 0.1 and 0.3 ppm, respectively. The toxic properties of bromine are somewhat similar to those of chlorine, but there are also significant differences.

Physiologically, bromine is an irritant gas. The effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema. Bromine is less soluble than ammonia, but more soluble than chlorine. It tends to attack the upper respiratory tract as well as the lungs, stripping the lining and, inducing suffocation. It also tends to cause more severe sublethal injury than chlorine.

Most work on bromine has been conducted in conjunction with work on chlorine, which has led experimenters to compare the toxicity of the two gases. Early work on bromine was carried out Lehmann (1887, 1893) and Hess (1911). Experiments conducted during the First World War are described by L. Hill (1915, 1920), Symes (1915a,b) and Chlopin (1927–). More recent work includes that by Rupp and Henschler (1967), Schlagbauer and Henschler (1967) and Bitron and Aharonson (1978). Work on bromine is also included in treatments dealing with a number of gases, including that of Haggard (1924).

From this work Withers and Lees (1986b) concluded that bromine is some 1.5 times as toxic as chlorine. Adopting essentially the same methodology as in their work on chlorine, described below, they give for the standard level of activity for the regular population the following probit equation for the lethality of bromine:

$$Y = -9.04 + 0.92 \ln L^* \qquad [18.16.1]$$

with

$$L^* = \Sigma C^2 T \qquad [18.16.2]$$

where C is the concentration (ppm), L^* is the toxic load (ppm^2 min) and T is the exposure time (min). This probit equation is discussed by P.C. Davies and Purdy (1987) and Withers and Lees (1987a).

Further probit equations for bromine have been given by ten Berge, Zwart and Appelman (1986), the CCPS and the CPD, as described below.

18.16.5 Carbon dioxide

Carbon dioxide is an asphyxiant, but also a toxic gas. It has long- and short-term OESs of 5000 and 15 000 ppm, respectively. At a concentration of 10% it can cause unconsciousness within 1 minute. It is odourless.

Hazard from the use of carbon dioxide in manufacturing arises where it is used in processes or where it is generated by combustion.

18.16.6 Carbon monoxide

Carbon monoxide is a chemical asphyxiant. It combines with haemoglobin in the blood, thus displacing the oxygen. It has long- and short-term OESs of 50 and 300 ppm, respectively. It is odourless.

Hazard from carbon monoxide arises where it is occurs as a process gas or where it is generated, as in combustion processes. Carbon monoxide is responsible for a significant proportion of deaths from gas poisoning.

18.16.7 Hydrocarbons

Hydrocarbons vary in toxicity. Some are asphyxiants, e.g. propane; others are assigned an OES, e.g. butane, which has long- and short-term OESs of 600 and 750 ppm, respectively.

18.16.8 Hydrogen chloride

Hydrogen chloride has a short-term OES of 5 ppm with no quoted long-term value. Physiologically, hydrogen chloride is an irritant gas. The effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema.

Early work on hydrogen chloride includes that by Lehmann (1886) and Hess (1911). Hydrogen chloride does not appear to have been a serious candidate war gas. More recent work includes that by Machle *et al.* (1942), Greenfield *et al.* (1969), Darmer, Kinkead and Dipasquale (1972, 1974), Nagao *et al.* (1972), Hilado and Furst (1976), Barrow *et al.* (1977), Hilado and Cumming (1978), Barrow, Lucia and Alarie (1979), Hartzell *et al.* (1985) and Hartzell (1989). Work on hydrogen chloride is also included in treatments dealing with a number of gases, including those of Haggard (1924), Higgins *et al.* (1972), MacEwen and Vernot (1972), Vernot *et al.* (1977) and Buckley *et al.* (1984).

The toxicity of hydrogen chloride has been reviewed in *Chlorine and Hydrogen Chloride* (WHO, 1982 EHC21).

Probit equations for hydrogen chloride have been given by Perry and Articola (1980), ten Berge, Zwart and Appelman (1986), the CCPS and the CPD, as described below.

Hydrogen chloride is one of the gases considered in the hazard assessment study of Back, Thomas and MacEwen (1972).

18.16.9 Hydrogen cyanide

Hydrogen cyanide has a short-term MEL of 10 ppm with no quoted long-term value. Physiologically, hydrogen cyanide is chemical asphyxiant. It causes cyanide poisoning, which is a form of asphyxia caused by the arrest of internal respiration. Its action can be very rapid.

Early work on hydrogen cyanide includes that by Geppert (1889), Matt (1889), Ahlmann (1905), Hess (1911), Fühner (1919), Drescher (1920), Koelsch (1920), Reed (1920), Hasselmann (1925a,b), Dschang (1928), R. Schwab (1929), Hug (1932), Wirth and Lammerhirt (1934) and Wirth (1935, 1937). Hydrogen cyanide was considered for use, but found little application, as a war gas, and its toxicity is dealt with in some of the texts on war gases, including those of F. Haber (1924), Vedder (1925), Ireland (1926), Flury and Zernik (1931), Foulkes (1934), Muntsch (1935), Hanslian (1937), Prentiss (1937), Wachtel (1941), Henderson and Haggard (1943) and by Flury (1921, 1928) and Chlopin (1927–). More recent work includes that of MacNamara (1976), Hilado and Furst (1976), Hilado and Cumming (1978), Hartzell, Priest and Switzer (1985) and Hartzell (1989). Work on hydrogen cyanide is also included in treatments dealing with a number of gases, including those of Schutze (1927), Walton and Witherspoon (1928) and Setterstrom and co-workers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940), Higgins *et al.* (1972) and Vernot *et al.* (1977).

Probit equations for hydrogen cyanide have been given by Perry and Articola (1980), ten Berge, Zwart and Appelman (1986), the CCPS and the CPD, as described below.

Hydrogen cyanide is one of the gases considered in the hazard assessment study done by Back, Thomas and MacEwen (1972).

18.16.10 Hydrogen fluoride

Hydrogen fluoride has a short-term OES (as F) of 3 ppm, with no quoted long-term value. Physiologically, hydrogen fluoride is an irritant and also has systemic effects. The irritant effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema. There is also evidence of systemic effects on organs including the liver, kidney, heart, spleen and thymus.

Hydrogen fluoride is subject to oligomerization, the extent depending on the pressure and temperature. At typical atmospheric conditions the apparent molecular weight is in the range 68–78.

Accounts of the properties of hydrogen fluoride are given by Muehlberger (1928), Simons (1931), Rushmere (1954), Maclean *et al.* (1962), Schotte (1987) and Clough, Grist and Wheatley (1987).

Early work on hydrogen fluoride includes that by Matt (1889), Ronzani (1908, 1909), Kehoe *et al.* (1932), Machle *et al.* (1934), Machle and Kitzmiller (1935) and Machle and Scott (1935) and Stokinger (1949). Hydrogen fluoride does not appear to have been a serious candidate as a war gas, but it is discussed by Flury and Zernik (1931) and Henderson and Haggard (1943). More recent work on the gas includes that by Rosenholtz *et al.* (1963), MacEwen and Vernot (1970), Darmer, Haun and MacEwen (1972), Hilado and Furst (1976), Hilado and Cumming (1978), Valentine (1988) and Mudan (1989a). Work on hydrogen fluoride is also included in treatments dealing with a number of gases, including those of Higgins *et al.* (1972), Wohlslagel, DiPasquale and Vernot (1976) and Vernot *et al.* (1977).

Probit equations for fatal injury by hydrogen fluoride have been given by Perry and Articola (1980), ten Berge, Zwart and Appelman (1986), Mudan (1989a), the CCPS and the CPD. Dangerous dose values are given by the HSE, as described below.

Mudan (1989a) derives his probit equation as follows. He utilizes primarily the more recent work of Rosenholtz *et al.*, MacEwen and Vernot, Darmer, Haun and McEwen, Higgins *et al.*, Wohlslagel, DiPasquale and Vernot, and the preliminary results of Valentine; MacEwen and Vernot give raw data, some of which is used by Darmer, Haun and MacEwen. From the results of these various workers he first establishes, using four data sets, that Haber's law applies, namely, ct = Constant. He then obtains LCt_{50} values of 26 880 ppm min for mice, 46 900 ppm min for small rats, 84 000 ppm min for large rats, 64 900 ppm min for guinea pigs and 106 440 ppm min for monkeys. Applying the toxicologist's rule-of-thumb that consistent results from three animal species may be applied to humans, he obtains for the latter the estimated LCt_{50} of 59 200 ppm min. Next he obtains separate probit equations for each of the species and from these a median best estimate of the slope of 4.853, thus yielding the desired probit equation:

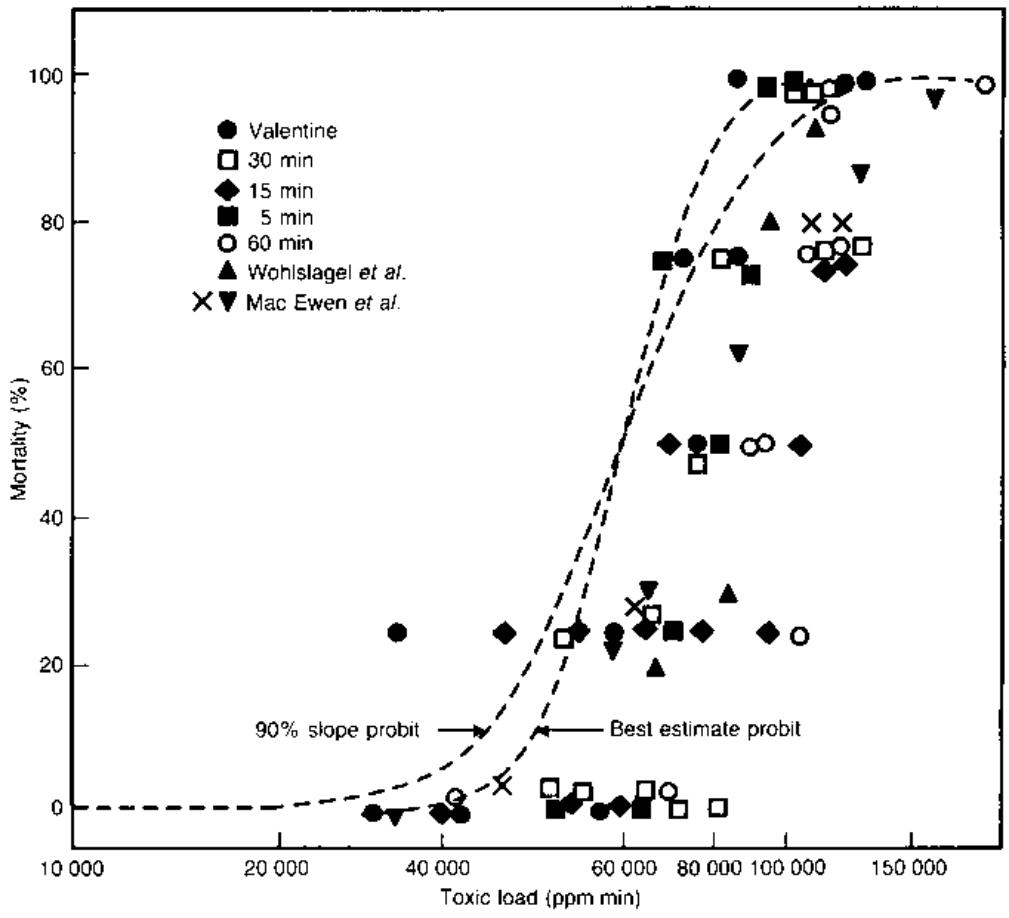

Figure 18.6 *Mortality–toxic load response from best estimate probit for hydrogen fluoride (Mudan, 1989a) (Courtesy of the American Institute of Chemical Engineers)*

$$Y = -48.33 + 4.853 \ln L^* \quad [18.16.3]$$

where

$$L^* = Ct \quad [18.16.4]$$

where C is the concentration (ppm) and t is the time (min). Mudan also determines the 90% confidence limits on the slope as 2.854 and 8.348. Using the lower value of the slope he obtains the further '90% slope probit' equation:

$$Y = -26.36 + 2.854 \ln L^* \quad [18.16.5]$$

The mortality given by these two probit equations is shown together with the experimental values in Figure 18.6.

Hydrogen fluoride is one of the gases considered in the hazard assessment study done by Back, Thomas and MacEwen (1972).

18.16.11 Hydrogen sulphide

Hydrogen sulphide has long- and short-term OESs of 10 and 15 ppm, respectively. Physiologically, hydrogen sulphide is an irritant and a chemical asphyxiant. The irritant effects of a single exposure include irritation of the mucous membranes, attack of the respiratory tract and pulmonary oedema. It also has an asphyxiant effect, caused by inhibition of cytochrome oxidase and resulting in arrest of respiration at the brain.

The gas can be detected at low concentration, but the sense of smell is lost after 2–15 minute exposure, thus making it impossible to detect dangerous concentrations. Moreover, the odour of hydrogen sulphide can be masked by the presence of other chemicals: tests have shown that concentrations below 1 ppm could be detected by odour in air, but in the presence of light hydrocarbons such as propane or butane even 5–10 ppm could not be smelt.

Early work on hydrogen sulphide includes that by Biefel and Pollock (1880), Lehmann (1892, 1893, 1899a),

Hess (1911), Haggard and Henderson (1922), Haggard (1925), C.W. Mitchell and Yant (1925), Gerbis (1927), Flury (1928), Aves (1929) and Yant (1930). Hydrogen sulphide was considered for use, but found little application as a war gas, and its toxicity is dealt with in some of the texts on war gases, including those of Vedder (1925), Flury and Zernik (1931), Foulkes (1934), Muntsch (1935), Hanslian (1937), Henderson and Haggard (1943) and by Flury (1928). More recent work on the gas includes that by Rubin and Arieff (1945), Adelson and Sunshine (1966), Lund and Wieland (1966), Kosmider, Rogala and Pacholek (1967), Hays (1972), Archibald (1977), Beck, Cormier and Donini (1979), NRC (1979), Tansy *et al.* (1981), Ammann (1986), Lopez *et al.* (1987), Prior *et al.* (1988) and Lopez *et al.* (1989). Work on hydrogen sulphide is also included in treatments dealing a number of gases, including those of Schutze (1927), Walton and Witherspoon (1928) and Setterstrom and co-workers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940) and Vernot *et al.* (1977).

The toxicity of hydrogen sulphide has been reviewed in *Hydrogen Sulphide* (WHO, 1983 EHC19).

Probit equations for hydrogen sulphide have been given by Perry and Articola (1980), ten Berge, Zwart and Appelman (1986), the CCPS and the CPD. Dangerous dose values are given by the HSE, as described below.

Hydrogen fluoride is one of the gases considered in the hazard assessment study done by Back, Thomas and MacEwen (1972).

18.16.12 Methyl isocyanate

Methyl isocyanate (MIC) has, like all isocyanates, long- and short-term MELs (as NCO) of 0.02 and 0.07 mg/m^3, respectively. Physiologically, MIC is an irritant and its effects include pulmonary oedema.

MIC came to prominence as the gas responsible for the toxic gas disaster at Bhopal, described in Appendix 5.

Prior to Bhopal, there seems to have been relatively little work published on the toxicity of MIC, with the exception of a study by Kimmerle and Eben (1964). Subsequent work has been done by ten Berge (1985). Probit equations for MIC have been given by ten Berge (1985), the CCPS and the CPD, as described below.

18.16.13 Oxides of nitrogen

Oxides of nitrogen are toxic gases. They have little irritant effect, but inhalation can cause death some hours later. Nitrogen monoxide has long- and short-term OESs of 25 and 35 ppm, respectively. Nitrogen dioxide has long- and short-term OESs of 3 ppm and 5 ppm, respectively.

Hazard from oxides of nitrogen arises from their use in the manufacture of sulphuric and nitric acids and from their generation in welding.

18.16.14 Phosgene

Phosgene has long- and short-term OESs of 0.02 and 0.06 ppm, respectively. Until recently the gas had a long-term OES of 0.1 ppm, with no quoted short-term value (see EH 40/92). The current values therefore represent a significant reduction.

Physiologically, phosgene is an irritant. The effects of a single exposure include pulmonary oedema. Phosgene is less soluble than chlorine, attacks the respiratory tract less, but passes deep into the lung. Its effects may not be felt immediately, but may develop some hours later.

Early work on phosgene includes that of Lehmann (1893), Matt (1889) and Hess (1911). Phosgene followed chlorine as a prime war gas, generally as a phosgene-chlorine mixture. Its toxicity is dealt with in most of the main texts on war gases including Underhill (1920), Fries and West (1921), Gilchrist (1924), F. Haber (1924), Vedder (1925), Ireland (1926), Flury and Zernik (1931), Foulkes (1934), Muntsch (1935), Hanslian (1937), Prentiss (1937), Wachtel (1941), Henderson and Haggard (1943), Courtice and Foss (1916), Dunn (1918), Eyster and Meek (1920), Herringham (1920), L. Hill (1920), Winternitz *et al.* (1920), Flury (1921a, 1928), Laqueur and Magnus (1921), Chlopin (1927–), Flury and Zernik (1932) and Richters (1936a,b). More recent work includes that by Cameron, Courtice and Foss (1941), Boyland, McDonald and Rumens (1946), Weston and Karel (1946, 1947), Box and Cullumbine (1947), Karel and Weston (1947), Gerard (1948), Suess and Lerner (1956), Henschler and Laux (1960), Ardran (1964), de Rooij, van Eick and van de Meent (1981), Diller and Zante (1982), Diller (1985), Mulder *et al.* (1986) and Zwart (1987). Work on phosgene is also included in treatments dealing with a number of gases, including those by Zeehuisen (1922) and Zielhuis (1970).

The toxicity of phosgene as a war gas has been the subject of extensive study. It was evidently his work on phosgene which led Haber to formulate his law that $ct =$ Constant. He expressed the toxicity of gases in terms of a mortality product, or lethal index. Haber (1924) himself gave for cats a value of 450 mg/m^3 of this index, whilst Wachtel gives a value of 900 mg/m^3. From analysis of comments by Flury and Zernik (1932), Withers and Lees (1985a) conclude that the value of 900 mg/m^3 is equivalent to the LCt_{50}. This corresponds to $LCt_{50} =$ 220 ppm min. They also quote Wachtel to the effect that cats are particularly sensitive to toxic gases and that as a rough approximation the corresponding value for man is twice as great, in other words $LCt_{50} = 440$ ppm min.

Experience of phosgene in war shows that personnel who have been gassed by it have often not felt immediate effects and have continued working, only to fall dead some hours later. The toxicity of phosgene has been reviewed in *Phosgene Toxicity Monograph* (MHAP, 1993).

Probit equations for phosgene have been given by Perry and Articola (1980), the CCPS and CPD, as described below.

Phosgene is one of the gases considered in the hazard assessment study done by Back, Thomas and MacEwen (1972).

18.16.15 Sulphur dioxide

Sulphur dioxide has long- and short-term OESs of 2 and 5 ppm, respectively. Physiologically, sulphur dioxide has various irritant effects.

Early work on sulphur dioxide includes that of Ogata (1884), Lehmann (1893) and Ronzani (1908, 1909). Sulphur dioxide does not appear to have been a serious candidate as a war gas. More recent work on sulphur

dioxide includes that of Leong, McFarland and Sellers (1961) and Bitron and Aharonson (1978). Work on sulphur dioxide is also included in treatments dealing with a number of gases, including those of Zeehuisen (1922), Setterstrom and co-workers (McCallan and Setterstrom, 1940; Thornton and Setterstrom, 1940; Weedon, Hartzell and Setterstrom, 1940), Zielhuis (1970) and Buckley *et al.* (1984).

Sulphur dioxide is a principal lethal component of smog such as that which was once prevalent in London. A thick fog which covered the Meuse Valley in Belgium in 1930 resulted in several hundred cases of severe respiratory disturbance, followed shortly after by 63 deaths which were attributed to it (Weedon, Hartzell and Setterstrom, 1939; Logan, 1953). The lethality of the 4 day London smog of December, 1952, has been studied by Anon. (1953) and Logan (1953). The latter attributes to the fog some 4000 deaths. The Los Angeles smog is described by A. Mills (1957).

Probit equations for sulphur dioxide have been given by Perry and Articola (1980), the CCPS and the CPD, as described below. An account is also given below of the HSE dangerous dose values for sulphuric acid mist.

Sulphur dioxide is one of the gases considered in the hazard assessment study of Back, Thomas and MacEwen (1972).

18.16.16 Toluene diisocyanate

Toluene diisocyanate (TDI), like all isocyanates, has long- and short-term MELs (as NCO) of 0.02 and 0.07 mg/m^3, respectively.

Physiologically, TDI has a systemic effect, attacking the nervous system. It is a sensitizer, carrying the notation 'Sen'. The effects of exposure may be immediate and/or delayed. Exposure to TDI can cause firefighters to become euphoric and disregard danger. Delayed effects include nervous disorders.

Hazard arises from its manufacture and use, and from its generation from polyurethane foam or in hot cutting operations.

18.17 Gas Toxicity: MHAP Studies

The toxicity of three gases – chlorine, ammonia and phosgene – is the subject of a set of monographs by the Major Hazards Assessment Panel (MHAP), convened under the auspices of the Institution of Chemical Engineers (IChemE).

18.17.1 Chlorine

The *Chlorine Toxicity Monograph* (MHAP, 1987) is in two parts: the First Report of the Working Party and an account by Davies and Hymes of the HSE of the approach by that body to the development of criteria for hazard assessment.

The working party review the data on chlorine toxicity. Many of the data quoted for humans are derivative and appear poorly founded. It is therefore necessary to resort to the use of animal data. The authors present data for the LC_{50} for different exposures and for a number of species. These animal data indicate a mean lethal concentration for a 30 minute exposure of $LC_{50} = 400$ ppm and a concentration–time relation of the form $ct^{\frac{1}{2}} = \text{Constant}$, or, alternatively $c^2t = \text{Constant}$.

In respect of the concentration lethal to man, the authors find that: the effects of acute inhalation of chlorine are similar in animals and humans, the prime lethal effect being pulmonary oedema; the factors bearing on differences between species may be divided into those which govern delivery of the chemical to the target organ and those which govern the effect on this and other organs; and that the effect of chlorine is to cause damage to the respiratory system itself, so that metabolic factors do not come into play.

The dose per unit body weight is some ten times greater for animals such as mice and rats than for humans at comparable levels of physical activity, but whereas humans are likely to respond to exposure to chlorine with a high level of activity, experimental animals are very passive. There is also the fact that rodents are obligatory nose breathers, which results in a degree of filtering and reduces somewhat the concentration reaching the respiratory tract, though the authors do not attach great importance to this feature. They conclude that there is little basis for supposing that the sensitivity of humans to chlorine is significantly different from that of small animals.

The working party suggest, therefore, that the relations for the lethal toxicity of chlorine quoted above for animals can be applied to humans also, namely for a 30 minute exposure:

$$LC_{50} = 400\,\text{ppm}$$
$$C^2t = \text{Constant}$$

where C is the concentration (ppm) and t is the time (min). They consider, however, that the data do not justify the derivation of a probit equation for the lethality of chlorine to humans.

The monograph also gives an account of medical measures for handling cases of gassing by chlorine and summaries of some 11 papers on its toxicity.

The contribution by Davies and Hymes states the, then developing, HSE view that for the purpose of land use planning a toxic load criterion corresponding to a much less severe level of injury than 50% lethality is appropriate and quotes the Major Hazards Assessment Unit (MHAU) as using for this purpose the criterion

$$C^{2.75}t = 3.2 \times 10^6 \qquad [18.17.1]$$

where C is the concentration (ppm) and t is the time (min). This echos the views expressed earlier by the same authors (P. Davies and Hymes, 1985) and foreshadows the development of the HSE specified level of toxity (SLOT) values described in Section 18.21.

18.17.2 Ammonia

The *Ammonia Toxicity Monograph* (MHAP, 1988) follows a broadly similar format. The data on ammonia toxicity are reviewed and animal data are presented for the LC_{50} for different exposures and for a number of species. These animal data indicate a lethal concentration for a 30 minute exposure of $LC_{50} = 11\,500$ ppm and a concentration-time relation of the form $ct^{\frac{1}{2}} = \text{Constant}$. The authors consider that for ammonia the animal data available are of higher quality than those for chlorine.

With regard to the applicability of these data to man, the authors advance the following argument. Like chlorine, ammonia has an irritant action, but due to its solubility the relative effect on the tracheal as opposed to that on the bronchial region is much more marked. They identify two opposing factors. On the one hand, there is the much higher dose per unit body weight in animals than in humans, but on the other, due to the less effective filtering in humans, a greater proportion of the gas will reach the trachea. The authors conclude that taking these factors into account, it is reasonable apply the animal data to humans.

They therefore propose that the relations for the lethal toxicity of ammonia quoted above for animals can be applied to humans also, namely:

$LC_{50} = 11\,500$ ppm for a 30 minute exposure

$$C^2t = 6.3 \times 10^4 \qquad [18.17.2]$$

They derive from this the probit equation for the lethality of ammonia

$$Y = -35.9 + 1.85 \ln C^2t \qquad [18.17.3]$$

where C is the concentration (ppm) and t is the time (min). They advise caution, however, in the application of this relation outside the limits of 20–80% lethality.

The monograph also gives an account of medical measures for handling of cases of gassing by ammonia, brief descriptions of case histories involving the gas and summaries of some 24 papers on its toxicity.

18.17.3 Phosgene

The *Phosgene Toxicity Monograph* (MHAP, 1993) again rejects many of the data quoted for humans as being second-hand and unreliable. The same applies to many of the animal data, but a small number of data sets are considered to be of high quality. These animal data indicate a lethal concentration–time relation of the form $ct =$ Constant, or Haber's law, and a lethal load of $LCt_{50} = 570$ ppm min.

The authors also refer to work on the gassing of human subjects by phosgene given in evidence by Bickenbach (1947). The experiments were barbarous, but the data exist and cannot be neglected. The median lethal concentration for a 25 minute exposure was 22.8 ppm, yielding $LCt_{50} = 570$ ppm min.

In respect of the application of the animal data to humans, the authors argue that the main acute effect of phosgene for both animals and humans is on the lung, that large differences in response between species would not be expected and that this is borne out by the similarity of the results obtained for the various species, including man. They conclude that the animal data may be applied to humans.

Utilizing the most appropriate sets of animal data and applying these to man, they obtain for the lethal toxicity of phosgene for humans

$LCt_{50} = 552$ ppm min

and the probit equation

$$Y = -27.2 + 5.1 \ln Ct \qquad [18.17.4]$$

where C is the concentration (ppm) and t is the time (min).

The monograph also gives an account of medical measures for handling of cases of gassing by phosgene and brief descriptions of case histories involving the gas.

18.18 Gas Toxicity: Chlorine

An further account is now given of the toxicity of chlorine, based on the work of Withers and Lees (1985a,b). This work is described in some detail, both because the hazard of chlorine is important in its own right and because the work illustrates the problems of and possible approaches to the toxicity of irritant gases.

There are in the literature a number of estimates of chlorine toxicity which vary widely. Generally, individual estimates are not well supported by critical review and the choice of a particular value has often tended to be arbitrary.

An estimate of chlorine toxicity which has had considerable currency in hazard assessment is that of Eisenberg, Lynch and Breeding (1975), who gave in the Vulnerability model a probit equation for chlorine. The LC_{50} for a 30 minute exposure given by this probit equation is about 35 ppm for healthy adults. More recent estimates tend towards a considerably higher figure.

Withers and Lees review information on the lethal toxicity of chlorine and present a model for its toxicity to humans. The model gives values of 500 and 250 ppm for the LC_{50} for 30 minutes for base and standard cases for healthy adults.

18.18.1 Experimental work on and estimates of toxicity

Data on chlorine toxicity are given by Flury and Zernik (1931). Many of the values quoted are attributed to Lehmann, who published a series of papers over the period 1887–99 (e.g. Lehmann, 1887, 1883, 1899a,b) and to Hess (1911).

Chlorine was the first main toxic gas used in the First World War and work on chlorine toxicity was carried out by the principal combatants, particularly the Germans. The German work is described by F. Haber (1924), Flury and Zernik (1931), Muntsch (1935) and Wachtel (1941).

Haber's work, apparently that on phosgene in particular, seemed to indicate for lethality the relation

$$ct = \text{Constant} \qquad [18.18.1]$$

which became known as Haber's law and gave rise to the concept of a lethal dosage, also known as the mortality product or lethal index.

Values of the lethal index are quoted by military authors such as Hanslian (1937), Vedder (1925) and Prentiss (1937). There are considerable variations in the values given. Withers and Lees suggest that values refer variously to the LC_{10}, the LC_{50} and the LC_{90}, and quote comments by Flury and Zernick (1932) in support of this.

An important series of experiments on dogs was carried out towards the end of the war by Underhill (1920). For chlorine he used some 112 animals in seven groups ranging in size from 9 to 23. The exposure period was 30 minutes. The results of this work are shown in Table 18.18 and are plotted in Figure 18.7. The figure shows the best line through the points and the 95% confidence limits obtained from the method of Litchfield

Table 18.18 *Concentration of chlorine lethal to dogs in Underhill's work (Withers and Lees, 1985a; after Underhill, 1920). Exposure time 30 minutes (Courtesy of Elsevier Publishing Company)*

	Concentration[a]						
(mg/l) (ppm)	*0.16–0.80 50–250*	*1.27–1.58 400–500*	*1.58–1.90 500–600*	*1.90–2.22 600–700*	*2.22–2.53 700–800*	*2.53–2.85 800–900*	*2.85–6.34 900–2000*
Deaths within 3 days	0	1	2	9	9	20	13
Delayed deaths	1	4	2	5	2	1	0
Total deaths	1	5	4	14	11	21	13
Total No. of animals	9	17	10	21	18	23	14
Overall mortality (%)	11	29	40	67	61	91	93

[a] The conversion of concentrations from mg/l to ppm by Underhill in this table corresponds to a temperature of 0°C. Henceforth, these concentration values in ppm have been recalculated to a temperature base of 25°C.

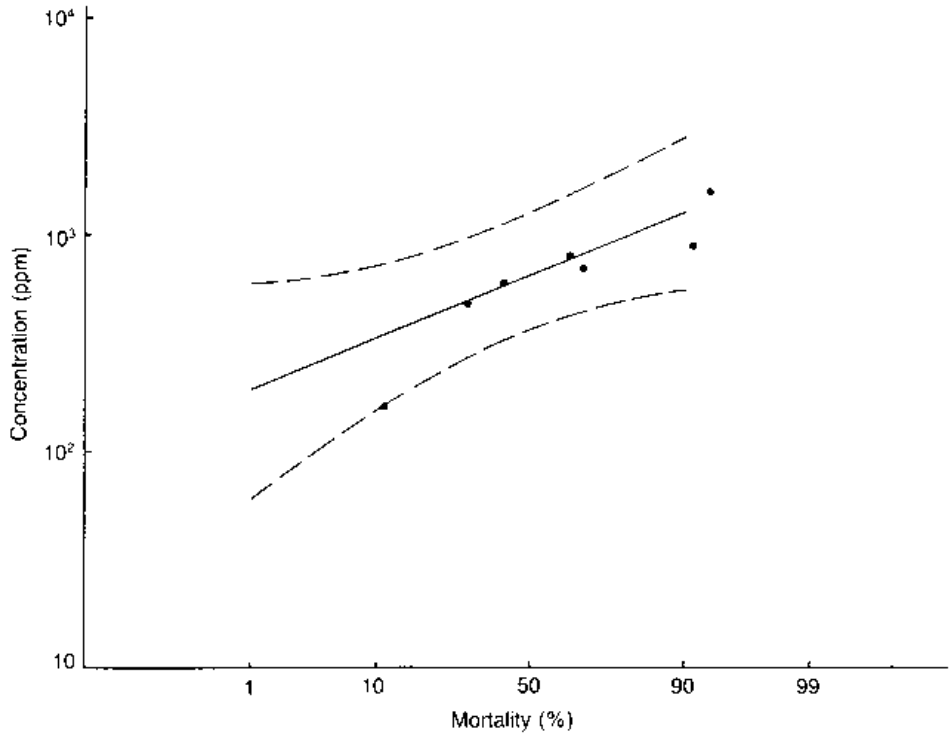

Figure 18.7 *Concentration of chlorine lethal to dogs in Underhill's work (Withers and Lees, 1985a; after Underhill, 1920). Exposure time 30 minutes. Dotted lines are 95% confidence limits (Courtesy of Elsevier Science Publishers)*

and Wilcoxson (1949). The LC_{50} for a 30 minute is 650 ppm.

Since 1918 there have been a number of studies on chlorine toxicity, using mainly rodents. Some of the principal sets of experiments are briefly described here. More detailed accounts are given by Withers (1986) and Withers and Lees (1985a).

Weedon, Hartzell and Setterstrom (1940) carried out experiments in which mice and rats, in groups of 4 and 8, respectively, were exposed to concentrations of

Table 18.19 *Concentrations of chlorine that are lethal to rodents, as given by various authors (Withers and Lees, 1985a) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Species*	*Concentration lethal to 50%* (ppm)	*Exposure time* (min)
Zeehuisen (1922)	Guinea-pigs, white rats	>3330	30
Weedon, Hartzell and Setterstrom (1940)	Mice	1000	28
		250	440
		63	>960
	Rats	1000	53
		250	440
		63	>960
Lipton and Rotariu (1941)	Mice	628	10
Silver and McGrath (1942); Silver, McGrath and Ferguson (1942)	Mice	618[a]	10
Elmes and Bell (1963); Bell and Elmes (1965)	Mice	117[b]	1800
Schlagbauer and Henschler (1967)	Mice	127	30
Back, Thomas and Macewen (1972)	Mice	137[c]	60
	Rats	293[c]	60
Bitron and Aharonson (1978)	Mice	290[d]	11
		170	55
Alarie (1980)	Mice	302	10

[a] Value obtained by averaging values of 524 and 597 ppm and then averaging again with value of 676 ppm.
[b] Exposure of 30 h limited to 3 h/day.
[c] These values are also given by Vernot *et al.* (1977)
[d] These values are for a 30 day observation period.

chlorine of 16, 63, 250 and 1000 ppm for periods of 1, 4, 15, 60, 240 and 960 minutes until they died, or for a maximum period of 960 minutes. The three latter concentrations corresponded to the LC_{50} for mice at exposure periods of >960, 440 and 28 minutes, respectively, and to that for rats at exposure periods of >960, 440 and 53 minutes, respectively.

Lipton and Rotariu (1941), in a report by Geiling and McLean, describe experiments in which mice in groups of 20 were exposed to concentrations of chlorine ranging from 310 to 2357 ppm for a period of 10 minutes with an observation period of 10 days. The LC_{50} obtained was 628 ppm.

Silver and McGrath (1942) carried out experiments on 49 groups of mice, 45 groups of 20 and 4 groups of 40, in two series. In the first series certain sources of error were revealed which were corrected in the second series. In the two series of experiments mice were exposed to concentrations of chlorine in the range 252–1,139 ppm for 10 min with a 10-day observation period. In the first series the LC_{50} was 524 ppm and in the second series 597 ppm. Most of the deaths occurred within the first 24 hours.

Silver, McGrath and Ferguson (1942) carried out further experiments on 15 groups of 20 mice. Again they used a 10 minutes exposure time and a 10-day observation period. In this third series the concentrations of chlorine used were in the range 379–890 ppm and the LC_{50} was 676 ppm. Out of 154 deaths, one was due to mild oedema and congestion, and two to pneumonia; the rest were due to severe oedema. Most of the deaths occurred within the first 24 hours.

Schlagbauer and Henschler (1967) carried out experiments in which mice in groups of 10 were exposed for

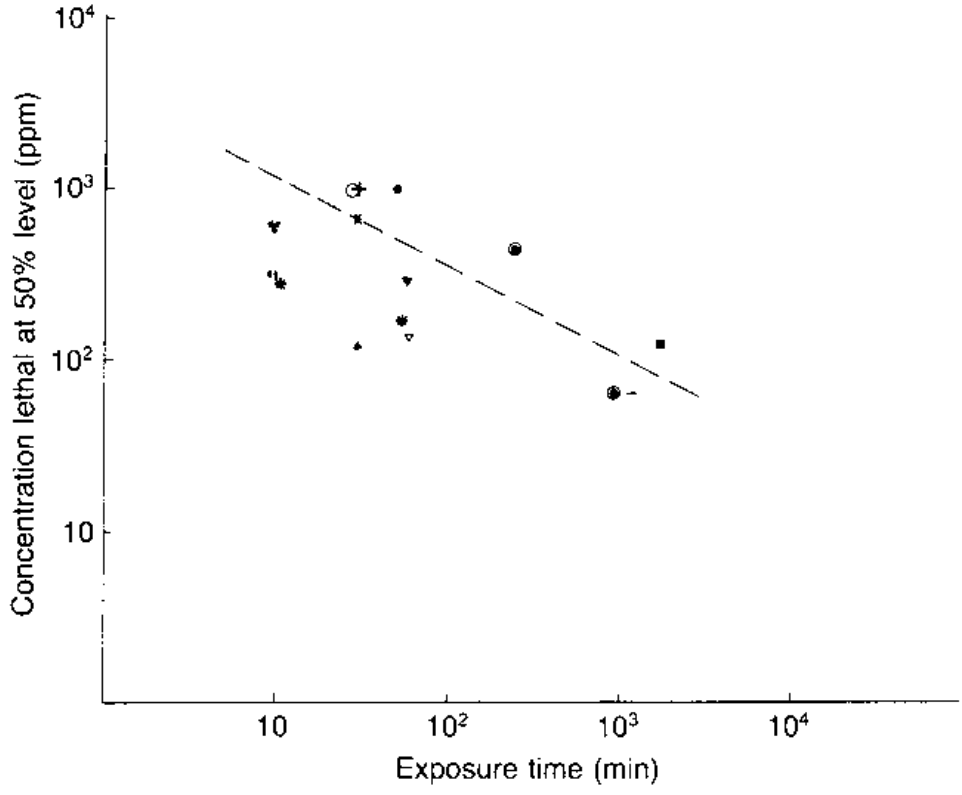

Figure 18.8 *Concentration of chlorine that is lethal to various animal species at the 50% level (Withers and Lees, 1985a). Dotted line has slope of −0.5. (○) Weedon et al. (1940), mice; (✾) Lipton and Rotariu (1941), mice; (□) Silver and Mcgrath (1942), Silver McGrath and Ferguson (1942), mice; (▲) Schlagbauer and Henschler (1967), mice; (▽) Back, Thomas and MacEwen (1972), mice; (✷) Bitron and Aharonson (1978), mice; (◐) Alarie (1980), mice; (●) Weedon et al. (1940), rats; (■) Bell and Elmes (1965), rats; (▼) Back, Thomas and MacEwen (1972), rats; (×) Underhill (1920), dogs; (+) Chlopin (1927-), horses (fatal concentration, not necessarily LC_{50}) (Courtesy of Elsevier Science Publishers)*

30 minutes to concentrations of chlorine of 55, 62, 69, 110, 125, 132, 145, 160 and 179 ppm. The deaths occurring in the intervals 0–2 and 2–4 days after exposure were recorded. There were no deaths later than 4 days after exposure. The LC_{50} obtained was 127 ppm.

These authors also report work at lower chlorine concentrations and longer exposure periods. They carried out experiments in which 10 mice were exposed for 3 hours to concentrations of chlorine of 10 and 22 ppm with an observation period of 4 days. The mortality of the mice at these two concentrations was 8/10 and 10/10, respectively.

Experiments were carried out by Bitron and Aharonson (1978) in which mice in groups of 16 were exposed to concentrations of chlorine of 170 and 290 ppm for periods of 15–160 and 5–30 minutes, respectively. The times of death after exposure were recorded over an interval of 30 days. The LC_{50} values obtained were 170 and 290 ppm for exposures of 55 and 11 minutes, respectively.

The LC_{50} values obtained by these and certain other authors are shown in Table 18.19. The concentration lethal to various animal species, based on the research just described and on other work, is shown in Figure 18.8.

In addition to the LC_{50}, it is desirable also to be able to estimate the LC_{10} and LC_{90} or the ratio LC_{90}/LC_{10}, which is the slope of the concentration–mortality line. There are three data sets, those of Underhill, of Silver, McGrath and Ferguson and of Schlagbauer and Henschler, from which estimates of this ratio may be obtained.

Underhill's work yields values of the LC_{10} and LC_{90} of 334 and 1266 ppm, respectively, and hence a value of the ratio LC_{90}/LC_{10} of 3.8.

There are two sets of experiments, those of Weedon, Hartzell and Setterstrom and of Bitron and Aharonson, in which the exposure time was varied and which may therefore be used to estimate the trade-off between concentration and time. These two data sets are shown in Table 18.20.

Table 18.20 *Concentrations of chlorine lethal to rodents at the 50% level as a function of time (Withers and Lees, 1985a) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Species*	*C* (ppm)	*T* (min)	*CT*	$CT^{0.4}$	$CT^{0.5}$	$CT^{0.6}$
Weedon, Hartzell and Setterstrom (1940)	Mice	1000	28	28 000	3792	5292	7 384
		250	440	110 000	2853	5244	9 639
	Rats	1000	53	53 000	4895	7280	10 828
		250	440	110 000	2853	5244	9 639
Bitron and Aharonson (1978)	Mice	290	11	3 190	757	962	1 222
		170	55	9 350	844	1261	1 882

Table 18.21 *Mortality of animals exposed to chlorine, adjusted to an exposure period of 30 minutes and normalized with respect the LC_{50} (Withers and Lees, 1985a) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Species*	LC_{50} (ppm)	*Concentration* (ppm)	*Normalized concentration*	*Mortality* (%)
Underhill (1920)	Dogs	650	164[a]	0.25	11
			491	0.76	29
			600	0.92	40
			710	1.09	67
			819	1.26	61
			928	1.43	91
			1583	2.44	93
Silver and McGrath (1942); Silver, McGrath and Ferguson (1942)	Mice	388	219[b]	0.56	10
			317	0.82	45
			317	0.82	25
			337	0.87	5
			364	0.94	40
			368	0.95	45
			398	1.03	15
			408	1.05	60
			410	1.06	55
			430	1.11	70
			458	1.18	75
			486	1.25	40
Schlagbauer and Henschler (1967)	Mice	131	62	0.47	10
			69	0.53	10
			110	0.84	30
			125	0.95	30
			132	1.01	60
			143	1.09	60
			160	1.22	80

[a] Converted from 0°C to 25°C.
[b] Converted from original data for 10 minutes exposure period.

Then using Equation 18.11.3 for the lethal toxic load, the data in Table 18.20 suggest that the best estimate of the index n is 0.5 so that

$$L = CT^{0.5} \qquad [18.18.2]$$

The range of concentrations and time covered by the data on which this equation is based are 170–1000 ppm and 11–440 minutes.

Equation 18.18.2 may be used to convert different sets of experiments to a common exposure time. Such sets may also be normalized with respect to the LC_{50} found in each case to give a set of data which may be used to determine the slope of the concentration–mortality line. Three such sets of data are shown in Table 18.21.

Information on acute and delayed deaths is also relevant. In the work of Lipton and Rotariu and of Silver, McGrath and Ferguson most of the deaths occurred within the first 24 hours. Likewise, in Schlagbauer and Henschler's work almost all the deaths occurred in the interval 0–2 days after exposure. The only deaths in the interval 2–4 days were at a

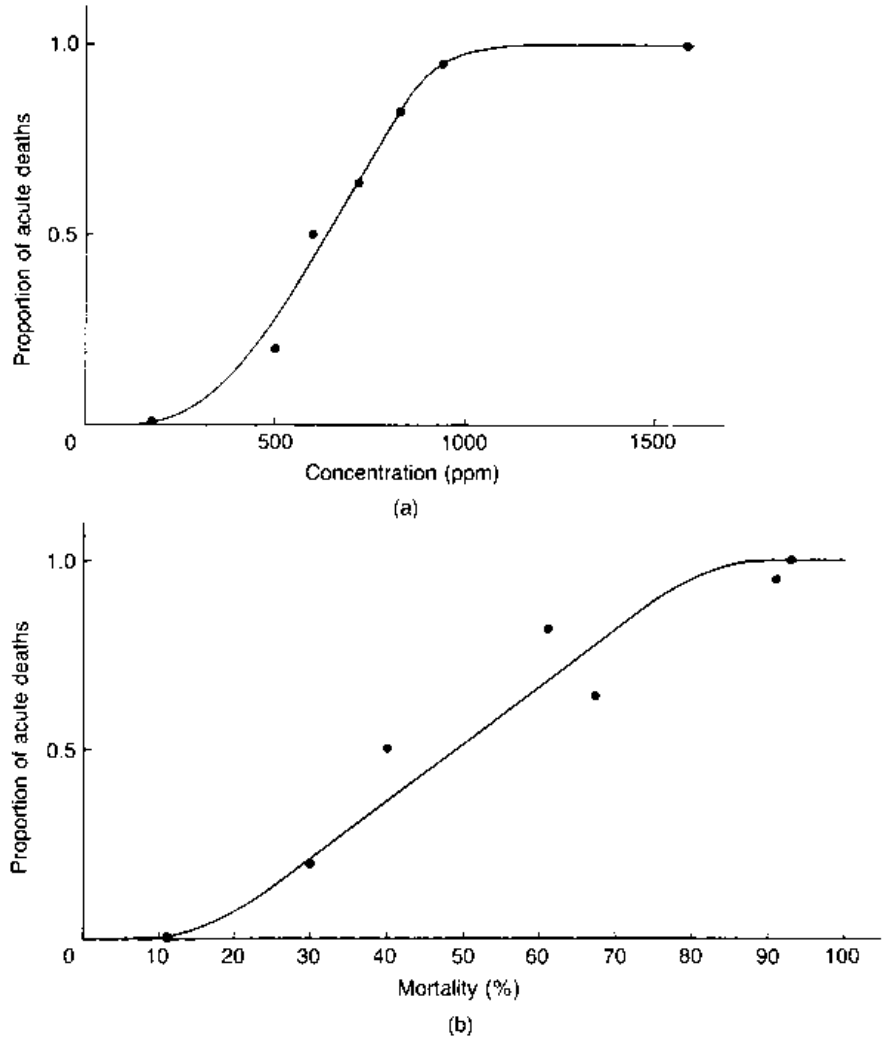

Figure 18.9 *Proportion of acute deaths by chlorine poisoning in Underhill's work (Withers and Lees, 1985a). Exposure time 30 minutes. (a) Proportion of acute deaths as a function of concentration; (b) proportion of acute deaths as a function of mortality (Courtesy of Elsevier Science Publishers)*

concentration of 132 ppm, for which 2 of the 6 deaths were in this interval. In Bitron and Aharonson's work, by contrast, most of the deaths were delayed deaths, the mortality being only 10% or less during the day after exposure and most of the deaths occurring in the interval 5–7 days after exposure.

Further information on acute deaths is given by the work of Underhill on dogs. He defines acute death as a death occurring within the first 3 days after exposure. Figures 18.9(a) and 18.9(b) shows the proportion of acute deaths in his work as a function of the concentration and as a function of the mortality, respectively.

18.18.2 Physiology and pathology of poisoning

The physiology and pathology of chlorine gas poisoning have been studied by a number of workers, including many of those already mentioned.

Many of those who have done experimental work on animals have discussed this aspect. Lehmann gives a wide-ranging discussion of the topic. Accounts by German workers active around the time of the First World War include those by Flury and Zernik (1931) and Wachtel (1941) and among American workers those of Underhill (1920) and Winternitz *et al.* (1920). The overall picture which emerges is that while chlorine attacks the whole of the respiratory system, the cause of death is lung oedema.

There is also a large amount of information which is directly applicable to man. There are a number of accounts of the treatment of chlorine gas casualties by British doctors. The Chemical Warfare Committee of the Medical Research Council did extensive work, including that of Gunn (1920) on the action of chlorine on the

respiratory system. The official military account is given in *Diseases of the War* (Macpherson *et al.*, 1923).

The extensive American work from that time is described by Underhill and Winternitz *et al.*, while the official military account is given by Ireland (1926). Additional information is given by Haggard (1924) and by Henderson and Haggard (1943). Further accounts are given by other military authors such as Vedder (1925) and Prentiss (1937).

Investigations of the long-term effect of gas warfare exposure are described by Meakins and Priestley (1919), Vedder (1925), Gilchrist and Matz (1933) and Penington (1954).

Chlorine is a strong oxidizing agent. A number of different explanations have been given of the way in which it causes damage. An early suggestion was that its effect is through the formation of hydrochloric acid. Another early suggestion was that it gives rise to nascent oxygen. More recent suggestions are the action of hypochlorous acid and of chlorine itself.

Chlorine is an irritant gas and the most serious effect of acute chlorine poisoning is damage to the respiratory system. Another important irritant gas which was also used as a war gas is phosgene and many discussions of gas poisoning treat the two gases together, although there are differences. The symptoms of chlorine poisoning are: at a concentration of about 15 ppm, irritation of the nose, throat and eyes with cough and tears; at about 30 ppm, restriction of breathing and chest pain; and from about 50 ppm, development of pulmonary oedema. Other symptoms are described in some of the accounts given below.

The description by Haggard (1924) of the action of irritant gases on the respiratory tract has already been quoted.

In the present context it is severe acute poisoning which is of primary interest. Herringham (1920) states:

> The whole course of events, and the various degrees of severity, are all due to but one cause, the want of oxygen in the blood due to the wall of oedema interposed between the air and the blood vessels.

An extensive discussion of chlorine poisoning is given in *Diseases of the War* and the following extracts give an overview of the principal aspects. The threat to life is due almost entirely to pulmonary oedema and other effects are relatively unimportant, but later infection can also be dangerous:

> The respiratory organs, eyes and skin, bore the brunt of the attack. Yet even if one recognizes this, one must be prepared for serious effects which are secondary to these primary lesions. Severe though temporary shortage of oxygen, resulting from acute pulmonary oedema or interference with the oxygen-carrying power of the blood, may exercise lasting effects on the heart, the central nervous system, or other organs of the body, while secondary bacterial infection may delay recovery or even be the prelude to a fatal termination.

> The points where the gases classed as acute lung irritants exercise their most pronounced effect are the alveoli of the lungs and the smaller bronchial tubes, and the great danger to be feared, which is common to them all, is the onset of acute pulmonary oedema. It is in the main this oedema which, in the acute stage of poisoning, threatens the life of the subject, for if abundant it causes death by asphyxiation, the patient being in fact drowned by his own eduction.

> The rate of onset and the degree of oedema are dependent on the particular gas and on its concentration, and, though in some cases to a less degree, on the duration of exposure.

> Any pathological changes found in organs of the body other than the lungs are really attributable to changes resulting secondarily from the gross damage in the respiratory apparatus, and from the consequent asphyxia, and that the direct effects of the gas are limited to the lungs and bronchial tubes.

The effect of oedema is to cause a reduction in the supply of oxygen to the blood:

> These gross changes in the lungs are responsible for serious interference with the gaseous exchange between blood and air, and the indications for asphyxia were obvious in all severe cases of poisoning by the acute lung irritant gases. The cases fell into two categories: the one was characterized by intense florid and deep cyanosis, with vascular congestion and engorgement of the veins, the other exhibited no venous engorgement but pallor akin to that seen in collapse, with grey or lilac-coloured lips and tongue. Both classes had the common feature that the colour of the blood indicated a grave deficiency of oxygen.

The symptoms tended to follow a common pattern:

> All the men gave a similar description of what they felt as the greenish-yellow fumes enveloped them. Immediate choking, coughing, gasping for breath and inability to speak proved the irritation and spasm of the respiratory tract. In many the eyes smarted and ran with water. Retching was at once experienced by some, but many did not vomit until an hour or two later. There was severe pain behind the sternum, which soon radiated outward on each side into the chest and added greater suffering to the distressed breathing. The throat burned and the dry mouth produced an intense sensation of thirst.

> Very soon the developing pulmonary oedema led to the phenomenon of oxygen shortage, with headache, a sense of weakness in the legs, and such lassitude that the men dropped prone upon the ground, the spasmodic violence of their respiratory efforts being then largely quietened.

> Milder cases in areas where the concentration of chlorine in the air was relatively low, suffered chiefly from lassitude and a great sense of fatigue . . .

The complete arrest of breathing due to spasm was not observed and is not regarded as an important factor:

> The question has often been discussed as to whether a man might be killed by immediate asphyxiation on the field through such a spasmodic closure of his larynx and bronchi that respiration was completely arrested. Sudden shock and collapse from extreme sensory irritation has been noted in animals immediately upon exposure to chloropicrin; and it might be that this factor would also play its part in determining early death upon the field. But

> no proof was ever obtained that a man has thus been choked to death on the field . . . If it ever did happen, it was of little practical importance. No medical officer in the trenches ever had the chance of attempting to treat such a case.

Pulmonary oedema and its effects are therefore the important factors:

> A rapid development of pulmonary oedema, interfering with gaseous respiration and also with the circulation itself, was probably always the actual cause of death.
>
> It is thought that the entire action of pulmonary irritants is exercised solely upon the surface layers of the body with which the gases come into contact, the early circulatory failure being caused only the influence of pulmonary oedema upon gaseous respiration and blood-flow and by 'shock'.

A similar picture emerges from the accounts of their work given by Underhill and by Winternitz *et al.* Acute death is associated with oedema and blood changes. Underhilll attributes the effects of oedema not so much to the blockage of oxygen transfer in the lung as to a decrease in the fluid content of the blood and a consequent increase in the solids content and viscosity and a reduction in the oxygen-carrying capacity.

Physical exertion following gassing can be dangerous, even for men apparently unaffected:

> When the tension of a gas attack had passed way, it sometimes happened that, among those who had been exposed to the irritant vapour but who had not reported sick, a man would stop working, complain that he felt done in, and die in a few minutes. Others might survive for an hour or two after a similarly sudden collapse. Their deaths were at first thought to have been caused by heart failure due to a direct intoxication by the gas. Autopsies, though not made in the dramatic cases of abrupt death, always proved the existence of advanced pulmonary oedema, the condition being really identical with that of 'grey' collapse as seen after the ordinary acute onset.

The effect of exertion after exposure appears, however, to have been observed mainly with phosgene rather than with chlorine.

There has been some expression of doubt about the prevalence of pulmonary oedema among those who have treated people gassed by chlorine in industrial accidents. Thus A.T. Jones (1952) states that in the period 1932–1948 he and his colleagues dealt with 820 such cases, of which 9 were severe, but that even in these cases neither pulmonary oedema nor pneumonia ensued, although he indicates awareness of pneumonia in other cases. Industrial gassing is also discussed by Haggard, who states

> Even an exposure insufficient to induce the acute symptoms of lung irritation may lead to the development of pneumonia and under industrial conditions the infections thus produced constitute a greater cause of death than primary oedema.

Although the descriptions quoted of the effect of irritant gases are undoubtedly strongly influenced by experience with phosgene, the account of Black, Glenny and NcNee (1915), who treated 685 cases of poisoning from chlorine between 2 and 7 May, 1915, before phosgene had been used, shows clearly that the acute deaths involved pulmonary oedema. This was confirmed by 210 post-mortems carried out by these doctors.

If acute death does not occur, there is still the danger of delayed death. The cause of delayed death is described variously as bronchitis, bronchial pneumonia or pneumonia. Black, Glenny and McNee state that the acute stage passes off in about 36 hours, that there is then a quiet stage of some 12 hours and that the bronchial infection is then liable to develop. Underhill found that the dogs which survived gassing were liable to die of pneumonia, and set 3 days after gassing as the dividing line between acute and delayed deaths.

The mortality from chlorine gassing may be reduced by appropriate medical treatment. It is not clear how much can be done to increase the chances of survival of acute cases, but for the delayed cases the prospects appear much better. There are descriptions of the treatment given and of its effects in many of the accounts already quoted.

The long-term effects of chlorine gassing are also important. Broadly speaking, both the statistical and clinical evidence suggest that these effects are not great. Weill *et al.* (1969) studied 12 people who were severely gassed in an accidental chlorine accident near La Barre in 1961. All had pulmonary oedema when examined just after the accident, but when examined 3 and 7 years after the event showed little long-term damage.

A summary of the findings of these authors given by Eisenberg, Lynch and Breeding (1975) has been quoted in Section 18.15. The evidence from this work is that persons who survive acute exposure to chlorine gas tend not to suffer significant permanent lung damage.

18.18.3 Concentrations intolerable to humans

Some values given in the literature for chlorine concentrations tolerable and intolerable to humans are shown in Table 18.22.

At concentrations of about 4 ppm irritation is said to be experienced and normal work to be impossible. Dangerous concentrations are variously given as 14–21 and 40–60 ppm for $\frac{1}{2}$–1 h, but the degree of danger is ill defined. A concentration of about 50 ppm is said to cause loss of fighting efficiency and one of 100 ppm to incapacitate and to be intolerable. The data were apparently obtained by observation of the effects of chlorine on man. The basis of the data is different, therefore, from those for the lethality to man derived from animal experiments. They include, presumably, the effects of any enhancement of activity which may have occurred.

18.18.4 Concentrations lethal to humans

Some values given in the literature of chlorine concentrations lethal to humans are shown in Table 18.23.

18.18.5 Limit values for humans

The TLV for chlorine recommended by the ACGIH has for many years been 1 ppm. In the UK the OES is now an 8–hour TWA of 0.5 ppm.

Table 18.22 *Concentrations of chlorine tolerable and intolerable to man (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Effect*	*Concentration* (ppm)	*Exposure time*	*Source*
Rupp and Henschler (1967)	Odour threshold	0.02–0.05		
ACGIH	Threshold limit value	1		
Kobert (1912)	Minimum concentration to detect odour	3.5		
	Concentration which causes immediate irritation	14		
	Concentration which causes coughing	28		
	Dangerous concentration	40	1 h	
Flury and Zernick (1931)	Concentration tolerable without immediate or later consequences	3.5	$\frac{1}{2}$–1 h	Lehmann–Hess[a]
	Concentration at which work can be continued without interference	1–2		Matt (1889)
	Concentration at which work becomes impossible	4		Matt (1889)
	Dangerous concentration	14–21	$\frac{1}{2}$–1 h	Lehmann–Hess[a]
Henderson and Haggard (1943)	Maximum concentration allowable for physical exertion	0.35–1		
	Minimum concentration to detect odour	3.5		
	Maximum concentration allowable for short exposure	4	$\frac{1}{2}$–1 h	
	Dangerous concentration for short exposure	40–60		
Vedder (1925)	Concentration which incapacitates man (crying, coughing) in a few seconds	100		
Wachtel (1941)	Concentration which causes severe irritation	3		
	Concentration which causes loss of fighting capacity	47		
Patty (1962)	Concentration which causes irritation	3–6		
	Intolerable concentration	100	1 min	

[a] Quoted without reference by Flury and Zernik (1931).

Zielhuis (1970) has made proposals for emergency exposure limits (EELs) for chlorine. His values are 7, 5, 4 and 3 ppm for exposures of 5, 15, 30 and 60 minutes, respectively. The proposals of the NAS-NRC (1973a) for public emergency limits (PELs) are 3, 2, and 2 ppm for exposures of 10, 30 and 60 minutes, respectively.

18.18.6 Probit equations given in literature

Probit equations both for lethality and non-lethal injury due to chlorine were given by Eisenberg, Lynch and Breeding (1975) in the Vulnerability model. The probit equation for the lethality of chlorine is

Table 18.23 *Lethal concentrations of chlorine quoted in standard toxicology texts (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Effect*	*Concentration* (ppm)	*Exposure time*	*Source*
Flury and Zernik (1931)	Lethal concentration for man	900 (2.5 mg/l)	Immediate	
	Lethal concentration for man	35–50 (0.1–0.15 mg/l)	$\frac{1}{2}$–1 h	Hess[a]
	Dangerous concentration for man	14–21 (0.04–0.06 mg/l)	$\frac{1}{2}$–1 h	Hess[a]
	Lethal concentration for man	1000	Short exposure	Kobert (1912)
	Dangerous concentration for man	40–60	Short exposure	Kobert (1912)
Patty (1962)	Lethal concentration for large animals	1000	After brief exposure	Flury and Zernik (1931)
	Concentration which may be lethal to cats	300	60 min	
	Concentration which is rarely lethal to dogs	650	30 min	
	Concentration which is never lethal to cats	280	30 min	
	Dangerous concentration for man	14–21	$\frac{1}{2}$–1 h	
Tatken and Lewis (1984)	LCL_0 mam[b]	500	5 min	Flury (1928)
	LC_{50} mus (mouse)	137	1 h	Back, Thomas and MacEwen (1972)
	LC_{50} rat	293	1 h	Back, Thomas and MacEwen (1972)
	LCL_0 gpg (guinea pig)	330	7 h	Lehmann (1887)
	LCL_0 cat	660	4 h	Lehmann (1887)
	LCL_0 dog	800[c]	30 min	Barbour (1919)
	LCL_0 hmn (man)	873	30 min	Prentiss (1937)
Sax (1984)	As Tatken and Lewis (1984)			
Henderson and Haggard (1943)	Lethal concentration	1000	Short exposure	
Matheson Co. (1961)	Lethal concentration	1000	After a few breaths	
Stahl (1969)	Dangerous concentration	20	30 min	

[a] Quoted without reference by Flury and Zernik (1931).
[b] Lowest lethal concentration recorded.
[c] A death was recorded in the concentration range 50–250 ppm (his values) at a 30 min exposure in Underhill's work (1920).

$$Y = -17.1 + 1.69 \ln(\Sigma C^{2.75} T) \quad [18.18.3]$$

and that for non-lethal injury due to chlorine is

$$Y = -2.40 + 2.90 \ln C \quad [18.18.4]$$

where C is the concentration (ppm) and T is the time (min).

Equation 18.18.3 gives an LC_{50} for 30 minutes of some 35 ppm. It is apparently derived from a graph consisting of an arbitrary concentration scale versus a percentage mortality scale on which various sets of experimental results for animals are plotted as straight lines. The LL_{50} points on these lines are: for dogs, 70; for rats, 3.5 and 1.4; for mice, 20, 15, 3.5 and 0.7; composite for all animals, 1; and for man, 0.25. It is not clear what the justification is for this low value for man, but the choice appears to be a conservative one.

In a further development of the Vulnerability model, Perry and Articola (1980) give revisions of the Eisenberg equations. Their equation for the lethality of chlorine is

$$Y = -36.45 + 3.13 \ln(\Sigma C^{2.64} T) \quad [18.18.5]$$

and that for chlorine injury is again Equation 18.18.4.

Table 18.24 *Some probit equations for chlorine given in the literature (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

A Equations for fatality				
		Lethal concentration for 30 min exposure period (ppm)		
		LC_{10}	LC_{50}	LC_{90}
Eisenberg, Lynch and Breeding (1975)	$Y = -17.1 + 1.69 \ln(\Sigma C^{2.75} T)$	26	34	44
Perry and Articola (1980)	$Y = -36.45 + 3.13 \ln(\Sigma C^{2.64} T)$	36	42	49
Rijnmond Report Industrial Comment (Rijnmond Public Authority, 1982); N.C. Harris and Moses (1983)	$Y = -11.4 + 0.82 \ln(\Sigma C^{2.75} T)$	237	418	738
ten Berge and van Heemst[a] (1983)	$Y = -5.04 + 0.5 \ln(\Sigma C^{2.75} T)$	170	430	1093
B Equations for injury				
Eisenberg, Lynch and Breeding (1975); Perry and Articola (1980)	$Y = -2.40 + 2.90 \ln C$			

[a] Original equation:
$Y = -6.5 + 0.5 \ln(\Sigma C^{2.75} T)$
where C is concentration (mg/m^3) and T is time (min).

The industrial comment on the *Rijnmond Report* (Rijnmond Public Authority, 1982) proposes the equation

$$Y = -11.4 + 0.82 \ln(\Sigma C^{2.75} T) \quad [18.18.6]$$

This equation is also recommended by N.C. Harris and Moses (1983). Ten Berge and van Heemst (1983) propose the equation (in the units used here)

$$Y = -5.04 + 0.5 \ln(\Sigma C^{2.75} T) \quad [18.18.7]$$

Harris and Moses effectively argue that there is no justification for taking a low value of the ratio of the lethal load for man to that of animals, or for assuming a very narrow spread of response, and set the parameters in Equation 18.18.6 accordingly. Ten Berge and van Heemst apparently derive their parameters from the work of Bitron and Aharonson (1978), together with information on the concentrations causing irritation in man.

The probit equations given in the literature for the lethal toxicity of chlorine are summarized in Table 18.24. Further probit equations produced subsequent to this study are described below.

18.18.7 Toxicity values used in hazard assessments

Some values of the lethal concentration or dosage of chlorine used in a number of hazard assessments are given in Table 18.25. Most correspond to an LC_{50} for 30 minutes of about 35 ppm. The much higher value of 430 ppm used by Meslin (1981) is an exception.

18.18.8 Model for humans

On the basis of the information just described, Withers and Lees (1985b) have derived for chlorine a model for the lethal toxicity to humans. The model is based on estimates for humans of the LC_{50}, the slope of the concentration–mortality line, or ratio LC_{90}/LC_{10}, and the lethal load function together with factors for inhalation rate and for medical treatment, and involves a separate treatment of the vulnerable population. Before considering the model proper, it is convenient to consider these latter aspects.

18.18.9 Physical activity

It is to be expected that man will not simply remain passive in the face of a toxic threat but will react by some form of physical activity such as seeking to escape or to obtain shelter.

There are two main effects of such activity. The first is that larger volumes of contaminated air are inhaled. Data on inhalation rates were given in Table 18.16**.** It is clear from these data that the inhalation rate is greatly increased by activity and that the factor can be as high as 15. The injury suffered as a result of more rapid inhalation is likely to be increased, and allowance needs to be made for this.

Table 18.25 *Values of the lethal concentration of chlorine used in various hazard assessments (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

Author(s)	*Effect*	*Concentration* (ppm)	*Exposure time* (min)	*Source*
Howerton (n.d., 1969)	Dangerous concentration[a]	35	Not defined	
Dicken (1974, 1975)	Fatal concentration[a]	90[b]	10	
		70	30	
		40	100	
	Dangerous concentration[a]	30	10	
		15	100	
Simmons, Erdmann and Naft (1973, 1974)	LD_{50}	1000 ppm min (say, 35 ppm for 30 min)		Chlorine Institute
Eisenberg, Lynch and Breeding (1975)	Lethal concentration LC_{50}	35	30	Self
Solomon, Rubin and Okrent (1976)	LD_{50}	40–60	30–60	
Meslin (1981)	Lethal dose	430	30	NIOSH
Rijnmond Public Authority (1982)	Lethal concentration LC_{50}	35	30	Eisenberg, Lynch and Breeding (1975)

[a] Concentration not further defined.
[b] Approximate values read from graph.

The other effect of enhanced activity is that larger amounts of oxygen are required by the body. Data on this aspect also were given in Table 18.16**.** This increased oxygen demand may occur during exposure and/or after exposure.

The level of physical activity is taken into account by defining a base level of activity, which corresponds to rest, and a standard level of activity which corresponds to a normal mixture of sitting, standing and moving about and for which the inhalation rate is twice that of the base level.

18.18.10 Inhalation rate

The effect of inhalation rate on the injury caused by a given concentration of chlorine in air is not obvious, but it is important because it is quite conceivable that high inhalation rates will increase the injury several-fold. The assumption made in the model is that over a given inhalation period injury is a function of the mass of chlorine absorbed.

The rate of absorption of chlorine in the lung is a mass transfer process and this process may be modelled. An account of the respiratory system, including quantitative data, was given in Section 18.13. The amount of chlorine absorbed is the product of the alveolar ventilation rate and the difference in the inhaled and exhaled chlorine concentrations. It is also equal to the product of the pulmonary diffusion capacity and the difference between the actual and equilibrium partial pressures of chlorine at the alveolar membrane wall. Finally, it is also equal to the sum of the amount of chlorine transported out of the lung capillaries by the blood and of that reacted in the alveolar tissue.

The situation with respect to the solubility of chlorine is complicated by the hydrolysis of chlorine to hypochlorous acid. The solubility of chlorine and its hydrolysis have been extensively studied and data are available on the solubility of unhydrolysed chlorine and on the equilibrium and rate constants for the hydrolysis. There do not appear to be any data on the solubility of chlorine in blood plasma, but the solubility of other gases such as oxygen, carbon dioxide and nitrogen is some 10% less in plasma than in water.

If it is assumed that the chlorine is simply absorbed into the blood, there will be a gradual accumulation of chlorine in the blood which will exert a corresponding equilibrium partial pressure at the alveolar membrane so that the concentration of chlorine in the blood will rise exponentially to an equilibrium value and absorption will tail off. However, this model does not appear to be consistent with the information available on the damage done to the body by chlorine. The evidence indicates that the damage is essentially confined to the lung.

A more appropriate assumption appears to be that the lung is a sink for the chlorine, which reacts with the alveolar tissue. This means that the venous blood entering the lung capillaries will contain very little chlorine. The maximum concentration of chlorine in the blood leaving the lung may then be obtained by solving the mass balance. Simple calculations based on the physiological parameters and the solubility of unhydrolysed chlorine indicate that for a man at rest the concentration of exhaled chlorine will be less than half the inhaled concentration. The actual value will be less than this maximum, since the concentration in the blood will be reduced both by hydrolysis and by reaction with

the tissues. Thus even at rest almost all the chlorine inhaled will be absorbed. This will also be true for moderate increases in physical activity, since the increase in inhalation rate is accompanied by an increase in the circulation of blood through the lungs.

Further support for this interpretation is afforded by experiments by Lehmann (1893), who measured the inlet and outlet concentrations of chlorine in chlorine-contaminated air breathed by men. The inlet concentration was 2 ppm, the outlet concentration was undetectable, the absorption thus being total. This evidence is not conclusive, since the chlorine concentration was low, but it points in the right direction.

As a first approximation, therefore, the inhalation rate is taken into account by defining a factor ψ_1 which is applied directly to the concentration in order to correct for inhalation rate.

18.18.11 Medical treatment

Appropriate medical treatment may effect a reduction in the mortality from exposure to chlorine. It is likely to be much more effective in preventing delayed deaths than acute deaths.

As described above, the proportion of acute deaths is a function of mortality. From analysis of war gas casualties the proportion P_a of acute to total deaths, or the acute death factor, is

$$P_a = 0.8 + 0.2P \qquad [18.18.8]$$

where P is the total mortality.

The effect of medical treatment is taken into account by defining a factor ψ_2 which is applied to the proportion of delayed deaths, or rather, in this context, potential delayed deaths, to yield the proportion of recoveries.

18.18.12 Vulnerable populations

So far consideration has been limited to the effect of toxic gas on healthy adults. A significant proportion of the population, however, is more vulnerable. It is necessary to distinguish, therefore, between the less vulnerable, or regular, population and the more vulnerable, or simply vulnerable, populations, which together make up the general, or average, population.

The principal categories of people vulnerable to chlorine gas are children, old people and people with respiratory or heart disorders. The less vulnerable members of the population are healthy youngsters and adults. The estimate given by Hewitt for the proportion of vulnerable people was given in Table 9.26. A rough value is some 25% of the population.

One approach which has been used in hazard assessment is that of Eisenberg, Lynch and Breeding, who used for chlorine and ammonia the relations between the general population and the vulnerable population given in Table 18.17. There are several points which should be noted in connection with this table. The general population is not well defined, particularly as to whether or not it includes the vulnerable population. Also it has been shown by Withers and Lees that the relations given imply a lower spread of lethal concentrations for the vulnerable than for the regular population.

The vulnerability of part of the population may be handled either by treating the whole population as a single homogeneous population with vulnerable members or by treating the regular and vulnerable sections as two populations. In the first approach there is a single distribution, whereas in the second there are two separate distributions with distinct modal values. It is not self-evident which approach is most likely to fit such data as may exist, but it is clear that for hazard assessment it is more convenient to handle the vulnerable population separately and to have a separate distribution applicable to that population. This is therefore the approach adopted. It may be noted, however, that if two distinct distributions are used, they do not in general yield a distribution of the same type for the average population. Specifically, if the distributions for the regular and vulnerable populations are both log–normal, that for the average population cannot be expected to be log–normal.

18.18.13 Lethal load

The different forms of the lethal load function have been described in Section 18.11. The lethal load functions used in the model are

$$L = CT^m \qquad [18.18.9]$$

and

$$L^* = \Sigma C^n T \qquad [18.18.10]$$

Equation 18.18.9 is the natural form for the correlation of the basic data, but Equation 18.18.10 is the more convenient for hazard assessment.

The animal experiments indicate for m a value of 0.5 and this is used in the model for humans. The corresponding value of n is 2.

18.18.14 Lethal concentration: regular population

In the model the estimate of the LC_{50} is based primarily on the judgement that the most weight should be given to the work on dogs by Underhill, and this is then interpreted in the light of the other animal experiments.

The animal experiments described above give average LC_{50} values for 30 minutes exposures of 256, 414 and 650 ppm for mice, rats and dogs, respectively. The LC_{50} used in the model for man is 500 ppm for 30 minutes for the regular population at the base level of activity.

The high weight given to Underhill's work on dogs is based on a number of factors. One is the similarity of the respiratory systems of dog and man. Another is the quality of the experimental work.

In Underhill's work the dogs tended to lie passively with their paws folded so that movement was minimal. This behaviour has been taken as corresponding to the base level of activity.

This estimate of the LC_{50} for man is intended to be a best estimate rather than a conservative one.

The slope of the concentration–mortality line, or ratio LC_{90}/LC_{10}, which is used in the model is 4. This also is based primarily on the value of 3.8 obtained from Underhill's work on dogs. The two other values obtained from the animal work are 4.4 (Silver and McGrath, 1942; Silver, McGrath and Ferguson, (1942) and 1.9 (Schlagbauer and Henschler, 1967) on mice.

The lethal load at the base level of activity then follows directly. For 50% mortality at a 30 minute exposure

$$LL_{50} = CT^{0.5} = 500 \times (30)^{0.5} = 2739 \text{ ppm min}^{\frac{1}{2}} \qquad [18.18.11]$$

Similarly, the lethal loads for 10% and 90% mortality are 1369 and 5477 ppm $min^{0.5}$, respectively.

18.18.15 Lethal concentration: vulnerable population

The lethal concentrations for the vulnerable population are based on an estimate that the LC_{10} for a 30 minute exposure for the vulnerable population at the base level of activity is 100 ppm. This estimate is derived partly from information derived from the animal experiments and partly from the concentrations reported as intolerable to man. In the experimental work on animals there was no fatality at a concentration below 50 ppm for a 30 minute exposure. The nearest approach was a single fatality at 62 ppm in Schlagbauer and Henschler's work. A concentration of 100 ppm is shown in Table 18.22 as being some four times that which causes coughing and equal to that which is intolerable or incapacitating.

It is also assumed in the model that the slope of the concentration mortality line, or ratio LC_{90}/LC_{10}, is the same as for the regular population. This gives for the vulnerable population values of 200 and 400 ppm for the LC_{50} and LC_{90} for 30 minutes.

18.18.16 Inhalation rate factor

The inhalation rate factor ψ_1 used in the model is the ratio of the inhalation rate at the actual level of activity to that at the base level, which corresponds to rest in bed and for which the inhalation rate is 6 l/min. This factor is applied directly to the inhaled concentration.

The normal, or standard, level of activity involves some movement and for this the inhalation rate is about 12 l/min. Thus for the standard level of activity $\psi_1 = 2$.

It is intended in the model that for the regular population the default level of activity be taken as the standard level, unless there is a reason to take some other level. For the vulnerable population the level of activity for old people and young children may approximate to the base level and the standard level, respectively.

18.18.17 Medical treatment factor

In the model the proportion of delayed deaths is estimated from Equation 18.18.8 and the effectiveness of medical treatment in converting delayed deaths into recoveries is accounted for using the medical treatment factor ψ_2. This is taken as 0.9 and 0.7 for the regular and vulnerable populations, respectively, which means that for these populations some 90% and 70% of the potential delayed deaths convert to recoveries. These are necessarily approximate estimates, but their overall effect on the mortality is not great, since most deaths are sudden rather than delayed.

It is not appropriate to claim credit for the mitigating effect of medical treatment unless there exist the organization, the expertise and the facilities commensurate with the accident envisaged.

18.18.18 Probit equations

From the foregoing the following probit equations may be derived:

Regular population

Base level of activity:

$$Y = -9.57 + 0.92 \ln(\Sigma C^2 T) \qquad [18.18.12]$$

Standard level of activity:

$$Y = -8.29 + 0.92 \ln(\Sigma C^2 T) \qquad [18.18.13]$$

Vulnerable population

Base level of activity:

$$Y = -7.88 + 0.92 \ln(\Sigma C^2 T) \qquad [18.18.14]$$

Standard level of activity:

$$Y = -6.61 + 0.92 \ln(\Sigma C^2 T) \qquad [18.18.15]$$

The lethal concentrations for exposure times of 10 and 30 minutes for the regular and vulnerable populations given in the model, as expressed in these probit equations, are shown in Tables 18.26 and 18.27, respectively.

Table 18.26 *Concentrations of chlorine proposed as lethal to humans for an exposure time of 10 minutes (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

A Regular population: standard level of physical activity

Concentration (ppm)	*Mortality* (%)	*Toxic load,* $CT^{0.5}$ (ppm $min^{0.5}$)
217	10	685
433	50	1369
866	90	2739

B Vulnerable population: standard level of physical activity

Concentration (ppm)	*Mortality* (%)	*Toxic load,* $CT^{0.5}$ (ppm $min^{0.5}$)
87	10	274
173	50	548
346	90	1095

C Average population: standard level of physical activity

Concentration (ppm)	*Mortality* (%)	*Toxic load,* $CT^{0.5}$ (ppm $min^{0.5}$)
139	10	438
364	50	1150
805	90	2547

18.18.19 Overall methodology

The overall methodology used in the model for the estimation of the mortality from an accidental chlorine release given the concentration–exposure time profile may be summarized as follows.

A straightforward estimate of the mortality for the regular and vulnerable populations with the standard level of activity may be obtained using Equations 18.18.13 and 18.18.15, respectively.

Table 18.27 *Concentrations of chlorine proposed as lethal to humans for an exposure time of 30 minutes (Withers and Lees, 1985b) (Courtesy of Elsevier Publishing Company)*

A Regular population: base level of physical activity

Concentration (ppm)	*Mortality* (%)	*Toxic load,* $CT^{0.5}$ (ppm $min^{0.5}$)
250	10	1369
500	50	2739
1000	90	5477

B Vulnerable population: base level of physical activity

Concentration (ppm)	*Mortality* (%)	*Toxic load,* $CT^{0.5}$ (ppm $min^{0.5}$)
100	10	548
200	50	1095
400	90	2191

C Regular population: standard level of physical activity

Concentration (ppm)	*Mortality* (%)	*Toxic load,* $CT^{0.5}$ (ppm $min^{0.5}$)
125	10	685
250	50	1369
500	90	2739

D Vulnerable population: standard level of physical activity

Concentration (ppm)	*Mortality* (%)	*Toxic load,* $CT^{0.5}$ (ppm $min^{0.5}$)
50	10	274
100	50	548
200	90	1095

E Average population: standard level of physical activity

Concentration (ppm)	*Mortality* (%)	*Toxic load,* $CT^{0.5}$ (ppm $min^{0.5}$)
80	10	438
210	50	1150
465	90	2547

If it is desired to derive an estimate which takes account of other conditions and makes at least some allowance for the other factors discussed, the approach is as follows:

(1) Estimate the inhalation rate factor and apply it to the concentration.
(2) estimate the toxic load using the corrected concentration;
(3) calculate the uncorrected mortality, estimate the acute deaths factor and apply it to this mortality;
(4) estimate the medical treatment factor and apply it to the proportion of potential delayed deaths;
(5) calculate the corrected mortality.

18.18.20 Gas warfare cross-checks

Since chlorine was the first major war gas, attempts have been made to cross-check estimates for the lethal toxicity of chlorine against the effects of gas attacks. One such attempt is that by Nussey, Mercer and Fitzpatrick (1986). Another is that by Withers and Lees (1987b, 1992) to check the model just described. Critiques of this work by R.F. Griffiths and Fryer (1988) and V.C. Marshall (1989b) have held that the uncertainties surrounding these attacks are simply too great to make a cross-check.

18.19 Gas Toxicity: *Green Book* Relations

Another, more recent, treatment of the toxicity of industrial gases is that given in *Methods for the Determination of Possible Damage* by the Committee for the Prevention of Disasters (CPD) in the Netherlands (1992b) (the *Green Book*) based on research by TNO. An account is given by de Weger, Pietersen and Reuzel (1991).

This work was preceded by the study of probit equations for individual species by ten Berge of Dutch State Mines (DSM) and Zwart and van Heemst of TNO (ten Berge, Zwart and Appelman 1986), to which reference has already been made.

In this methodology a distinction is made between locally acting substances and systemically acting substances.

18.19.1 Locally acting substances

For a locally acting substance the specific dose D'' is defined as

$$D'' = D/A \qquad [18.19.1]$$

where A is the surface area of the lungs (m^2), D is the inhaled dose (mg) and D'' is the inhaled dose per unit area of lung (mg/m^2).

The dose D is taken as

$$D = (V_a/1000)Ct \qquad [18.19.2]$$

where C is the concentration of gas in the atmosphere (mg/m^3), t is the exposure time (min) and V_a is the minute volume (l/min).

From empirical physiological relations

$$V_a \propto W^{0.70} \qquad [18.19.3]$$

$$A \propto W^{0.92} \qquad [18.19.4]$$

where W is the body mass (kg).

Then from Equations 18.19.2–18.19.4

$$D'' \propto W^{-0.22} \qquad [18.19.5]$$

The body masses of man, the rat and the mouse are 70, 0.3 and 0.03 kg, respectively. It follows then from relation 18.19.5 that the load on a rat and on a mouse are, respectively, some 3.3 times and 5.5 times that on a man.

This treatment has not allowed for absorption of gas in the air passages. Little such absorption occurs in humans, but most test animals are nose breathers and absorption occurs to a much greater degree.

There is considerable uncertainty as to whether the same dose per unit area of lung has the same effect on humans and animals. A safety factor f of 5 is applied to allow for this.

18.19.2 Systemically acting substances

For a systemically acting substance the specific dose D' is defined as

$$D' = D/W \qquad [18.19.6]$$

where D' is the inhaled dose per unit body mass (mg/kg).

In this case the mass absorbed is proportional to the oxygen consumption rather than the minute volume. Oxygen consumption is in turn, a function of body weight, being proportional to $W^{0.7}$ as in relation 18.19.3. Hence from relations 18.19.2, 18.19.3 and 18.19.6

$$D' \propto W^{-0.3} \qquad [18.19.7]$$

Then using the same body masses as before, relation 18.19.7 implies that the load on a rat and on a mouse are, respectively, some 5.1 times and 10.2 times that on a man.

There is uncertainty as to whether the same dose per unit body mass has the same effect on humans and animals. In this case a safety factor f of 10 is applied.

18.19.3 Extrapolation factor

The foregoing treatment incorporates certain safety factors, of 5 for locally acting substances and 10 for systemically acting ones. The dose values apply to inhalation rates for persons at rest. A further safety factor of 2 is then applied which allows for increased inhalation rates in the population during a toxic gas emergency.

An extrapolation factor f_d is now determined for extrapolation of results from each species to humans. Thus, for example, for a rat:

Load animal f_d = *Load man*	*Safety factor*	*Extrapolation factor*	
Local effect	3.3	5×2 0.33 0.25	0.25
Systemic effect	5.1	10×2 0.26 0.26	

The LC_{50} value for humans is obtained by multiplying the LC_{50} value for the test animal by the extrapolation factor. Values of the extrapolation factor f_d are as follows: rat, 0.25; mouse, 0.5; guinea-pig, 0.2; and hamster, 0.3.

18.19.4 Probit equations

Probit equations for use in hazard assessment are then derived as follows. The basic approach is to assume a value for k_2 in Equation 18.11.6 and, if necessary, a default value of n, and to determine the constant k_1 from animal LC_{50} data.

The constant k_2 is assigned a value of 1.0 in all cases. This corresponds to a high value of the ratio LC_{95}/LC_{05}, and for concentrations below the LC_{50} is the conservative assumption. For the index n the default value used is 2.

Then starting from an animal LC_{50} value for some time t, the first step is to obtain the LC_{50} for 30 minutes. This is then converted to a 30-minute LC_{50} for humans by application of the extrapolation factor f_d.

Where there are data for more than one animal species, a further step is taken. This is to obtain the average animal 30-minute LC_{50} and to multiply it by a factor of 2 before applying the extrapolation factor f_d to obtain the 30-minute LC_{50} for humans. This has the effect of reducing the overall safety factor which is applied.

The probit equations obtained are considered further in Section 18.20.

18.20 Gas Toxicity: Probit Equations

As described above, probit equations are available for a number of the toxic gases of industrial interest. They include in particular the collections given for the Vulnerability model by Perry and Articola (1980), in the *QRA Guidelines* by the CCPS (1989/4) and in the *Green Book* by the CPD (1992b). The limitations of probit equations have been discussed in Chapter 9 and need not be rehearsed here.

In addition to the inherent limitations of probit equations, it is also necessary to consider in each particular case both the situation to which it is intended to apply and the degree of conservatism incorporated. The basic data are generally obtained from experiments on animals which tend to remain passive, but the use of the correlation is presumably for humans in an emergency situation. In some cases the probit equation is explicitly conservative, whilst in others it is not, reflecting a difference of philosophy as to the point at which any safety factor should be applied.

Table 18.28 gives the parameters for probit equations for industrial toxic gases.

18.21 Gas Toxicity: HSE Dangerous Dose

As described in Chapter 9, the HSE use for the purpose of land use planning the concept of a 'dangerous dose'.

For toxic substances the interpretation of the dangerous dose concept and the methodology by which a value is derived is described in *Assessment of the Toxicity of Major Hazard Substances* (R.M. Turner and Fairhurst, 1989a).

The authors discuss the paucity of data on the effect of toxic gases on man and the problems of probit equations. They propose for land use planning the use not of probit equations but of a toxic load value which they call the specified level of toxicity (SLOT). This is expressed in the form of an equation for the dangerous toxic load (DTL) and of a set of values for the SLOT computed from this relation.

The SLOT is defined as a value associated with a situation in which: (1) almost all persons suffer severe distress; (2) a substantial fraction require medical attention; (3) some persons are seriously injured, requiring prolonged treatment; or (4) any highly susceptible person might be killed. Typically the SLOT used corresponds to a mortality of 1–5%. The SLOT selected

Table 18.28 *Parameters in probit equations for lethality for some principal industrial toxic gases*

Substance	*Probit equation parameters*[a]					
	CCPS[b]			CPD[c]		
	k_1	k_2	n	k_1	n	*30–min* LC_{50}
Acrolein	−9.931	2.049	1	−4.1	1.0	304
Acrylonitrile	−29.42	3.008	1.43	−8.6	1.3	2533
Ammonia[d]	−35.9	1.85	2	−15.8	2.0	6164
Benzene[e]	−109.78	5.3	2	–	–	–
Bromine[e]	−9.04	0.92	2	−12.4	2.0	1075
Carbon monoxide[e]	−37.98	3.7	1	−7.4	1.0	7949
Carbon tetrachloride	−6.29	0.408	2.5	–	–	–
Chlorine[d]	−8.29	0.92	2	−14.3	2.3	1017
Ethylene oxide[e]	–	–	–	−6.8	1.0	4443
Formaldehyde[e]	−12.24	1.3	2	–	–	–
Hydrogen chloride	−16.85	2.0	1.00	−6.7	1.0	3940
Hydrogen cyanide	−29.42	3.008	1.43	−9.8	2.4	114
Hydrogen fluoride[d]	−35.87	3.354	1.00	−8.4	1.5	802
Hydrogen sulphide	−31.42	3.008	1.43	−11.5	1.9	987
Methyl bromide	−56.81	5.27	1.00	−7.3	1.1	3135
Methyl isocyanate[e]	−5.642	1.637	0.653	−1.2	0.7	57
Nitrogen dioxide[e]	−13.79	1.4	2	−18.6	3.7	235
Phosgene	−19.27	3.686	1	−0.8	0.9	14
Propylene oxide	−7.415	0.509	2.00	–	–	–
Sulphur dioxide	−15.67	2.10	1.00	−19.2	2.4	5784
Toluene	−6.794	0.408	2.5	–	–	–

[a] Both sets of parameters are for toxic gas fatality probit equations of the form

$$Y = k_1 + k_2 \ln(c^n t)$$

where t is the time (min). In the CCPS equation (and in those of Perry and Articola (1980)) the units of concentration c are ppm, whilst in the CPD equation the units are mg/m^3.

[b] CCPS *QRA Guidelines* (1989/5). Except as described in (d) and (e) below, these are the values given by Perry and Articola (1980), who discuss the derivations.

[c] CPD *Green Book* (1992b); de Weger, Pietersen and Reuzel (1991). In all cases $k_2 = 1$.

[d] Perry and Articola give:

Ammonia: $k_1 = -28.33$; $k_2 = 2.27$; $n = 1.36$;
Chlorine: $k_1 = -36.45$; $k_2 = 3.13$; $n = 2.64$;
Hydrogen fluoride: $k_1 = -25.87$; $k_2 = 3.354$; $n = 1.00$.

[e] Perry and Articola do not give values for these substances.

depends, however, on the substance, and in some cases it may be appropriate to use several SLOTs.

Essentially the SLOT is a criterion for individual risk. For societal risk the authors refer to the use of the method described by Poblete, Lees and Simpson (1984) and extended by Lees, Poblete and Simpson (1986), which is described in Chapter 9.

The methodology described by Turner and Fairhurst for the derivation of a SLOT is broadly as follows. Since there is a lack of toxicity data for humans, it is necessary to resort to the use of data from experiments on animals. The most reliable data generally relate to the LC_{50} values and the associated exposure times, and it is this which is taken as the starting point. Data are gathered for a number of species and usually the data adopted are those for the most sensitive species. Next, estimates are made of the LC_{05} or LC_{01} values. In some cases the data available permit an extrapolation based on probits. If this is not possible, an alternative approach is to use an empirical value of the ratio LC_{50}/LC_{05}, or LC_{50}/LC_{01}, as the case may be.

At this stage, therefore, the method yields a single value of the SLOT LC_{05} or LC_{01} with an associated exposure time. It is then necessary to determine the trade-off between the concentration c and the time t, or, in other words, the value of the index in the toxic load $c^n t$. Essentially this requires data on concentration vs time for a given level of effect, such as the LC_{50}. The authors warn against the use for this purpose of values from different sets of experiments on different species, since the results may then owe more to differences between species than to differences in exposure time.

The SLOTs obtained are then correlated as a DTL equation. These SLOTs and the DTL are applicable to an animal species. Collateral evidence may then be sought to confirm that it is reasonable to apply the relation to humans.

Table 18.29 *HSE DTL and SLOT values for some principal industrial gases*

	Acrylonitrile	*Ammonia*	*Chlorine*	*Hydrogen fluoride*	*Hydrogen sulphide*	*Sulphuric acid mist*
MW	53.06	17.03	70.9	20.0	34.1	98.1
Boiling point (K)	350.3	−33.42°C	328.4	292.5	211.2	563–603
Freezing point (K)	189.5	−77.74°C	172	190	187.5	283[c]
Conversion factor (ppm → mg/m^3)[a]	2.2	0.7	2.9	0.83	4.4	
DTL	9600 ppm min	3.76×10^8 ppm^2 min	108 000 ppm^2 min	2 400 000 ppm^2 min	2×10^{12} ppm^4 min	2.16×10^5 (mg/m^3) min
SLOT values (ppm)[b]						
5 min	1920	8670	147	693	800[d]	208 mg/m^3
10 min	960	6130	100	490	669	147 mg/m^3
30 min	320	3540	60	283	508	85 mg/m^3
60 min	160	2500	42	200	427	60 mg/m^3
120 min	80	1770	30	141	359	42 mg/m^3
240 min	40				302	
480 min						21 mg/m^3

[a] Conversion factor for vapour at temperature 25°C and pressure 1.0133×10^5 Pa, except for hydrogen fluoride for which the conversion is based on 0°C.
[b] Units for all gases except for sulphuric acid mist, for which the units are mg/m^3.
[c] Value for 100% acid.
[d] Ceiling value for exposure period 0–5 min.

One feature of this approach is that the use of an LC_{05} or LC_{01} rather than an LC_{50} value means that there is more likely to be some data on humans which can be used as collateral evidence. Another feature is that, insofar as the animal data used are generally for the most sensitive species, the approach may be regarded as conservative.

The application of this methodology is now illustrated for a number of industrial toxic gases. Table 18.29 shows for these gases some physico-chemical properties and the SLOT and DTL values. Each of the studies described gives a table detailing results of single exposure inhalation studies in animals and a table of LC_{50} values for different species.

The accounts given below are necessarily brief summaries; the arguments adduced in support of the values chosen are much fuller in the original references and these should be consulted.

18.21.1 Acrylonitrile

The SLOT values for acrylonitrile are derived in *Toxicology of Substances in Relation to Major Hazards: Acrylonitrile* (R.M. Turner and Fairhurst, 1989b). The gas has an irritant effect.

The experimental data for animals are sparse and most are for long exposures; none were found for exposure periods of less than 30 minutes. The more sensitive species were dogs, in work by Brieger, Rieders and Hoders (1952), and mice, in work by Knobloch *et al.* (1971). From the data for these species the authors derive the single SLOT value of 40 ppm for 4 hours. They do not give a precise interpretation of this SLOT, but it would appear to correspond to a value of the order of LC_{05} to LC_{01}. They make use of several studies which bear on the relation between concentration and time and settle on a value of $n = 1$. The resultant SLOTs and DTL equation are then as given in Table 18.29.

18.21.2 Ammonia

The SLOT values for ammonia are derived in *Toxicology of Substances in Relation to Major Hazards: Ammonia* (Payne, Delic and Turner, 1990). Ammonia is an irritant gas which, being highly soluble, tends to attack the upper respiratory tract, causing laryngeal oedema, as well as pulmonary oedema. The authors suggest that reported cases of laryngeal spasm probably involved laryngeal oedema. The essential toxic effect is therefore irritation.

For ammonia there is a considerable amount of experimental data on animals. The most sensitive species is the mouse, but the authors also make some use of data for rats. For mice, the work of Silver and McGrath (1948) yields an LC_{50} of 10150 ppm for a 10 minute exposure and that of Kapeghian *et al.* (1982) an LC_{50} of 4230 ppm for a 60 minute exposure. From work on rats by Appelman, ten Berge and Reuzel (1982) a value of the index $n = 2$ may be obtained. It happens that this value of $n = 2$ is also consistent with the two LC_{50} values just mentioned. Data from these same studies were used to estimate values of the LC_{05} and LC_{01}. The resultant values for the LC_{01} are 6129 and 3296 ppm, respectively. Adopting the former and utilizing the value of n quoted yields the SLOTs and DTL equation given in Table 18.29.

18.21.3 Chlorine

The SLOT values for chlorine are derived in *Toxicology of Substances in Relation to Major Hazards: Chlorine* (R.M. Turner and Fairhurst, 1990a). The gas has an irritant effect.

For chlorine there is a considerable amount of experimental data on animals. The mouse appears the most sensitive species. For mice, the work of Schlagbauer and Henschler (1967) gives an LC_{50} of 127 ppm for a 30 minute exposure. Data from this study were used to estimate values of the LC_{05} and LC_{01} for this exposure time, the values obtained being 70 and 56 ppm, respectively. The index n is obtained from a critical review of the large variety of values quoted in the literature, the authors settling on $n = 2$. The resultant SLOTs and DTL equation are then as given in Table 18.29.

The generally conservative nature of the approach taken is illustrated in this case. The LC_{50} value derived from the work of Schlagbauer and Henschler on which the SLOTs are based is towards the lower end of the range of LC_{50} values for animals given in the literature.

18.21.4 Hydrogen fluoride

The SLOT values for hydrogen fluoride are derived in *Toxicology of Substances in Relation to Major Hazards: Hydrogen Fluoride* (R.M. Turner and Fairhurst, 1990b).

Hydrogen fluoride is an irritant gas, but it also has some systemic effects. Whilst there is little information on the long-term effects of a single non-lethal exposure, the general toxicological properties of the gas point to the possibility of permanent injury.

For hydrogen fluoride there is a limited amount of experimental data on animals, the most sensitive species being the mouse. The work of Wohlslagel, DiPasquale and Vernot (1976) gives for mice an LC_{50} of 342 ppm for a 60 minute exposure. Using data from this same study, Turner and Fairhurst obtain for the LC_{05} and LC_{01} at this same exposure time values of 230 and 205 ppm, respectively. From work on rats by Rosenholtz *et al.* (1963) they derive a value of the index $n = 2$. This then yields the SLOTs and DTL equation given in Table 18.29.

18.21.5 Hydrogen sulphide

The SLOT values for hydrogen sulphide are derived in *Toxicology of Substances in Relation to Major Hazards: Hydrogen Sulphide* (R.M. Turner and Fairhurst, 1990c).

In addition to being an irritant gas hydrogen sulphide also causes inhibition of intracellular respiration. The second of these effects grows in relative importance as the concentration increases.

For hydrogen sulphide the limited amount of experimental data on animals available show reasonable consistency. Turner and Fairhurst distinguish several concentration regions: 750–100 ppm; 450–750 ppm and 200–350 ppm. High concentrations, in the range 750–1000 ppm, cause rapid unconsciousness and death within a few minutes. The authors therefore take 800 ppm as a ceiling value, independent of exposure time. From examination of data on a number of species, including work by Prior *et al.* (1988) and Tansy *et al.* (1981), the authors obtain the following LC_{50} estimates: 300 ppm for 4 hours; 400 ppm for 60 minutes; and 500 ppm for 30 minutes. This set of values corresponds to a value of the index of $n = 4$. In the study by Prior *et al.* for an exposure time of 4 hours the LC_{50} was 501 ppm and the LC_{10} was 422 ppm, giving an LC_{50}/LC_{10} ratio of 1.19, which was then used to obtain the SLOTs. The resultant SLOTs and DTL equation are then as given in Table 18.29.

18.21.6 Sulphuric acid mist

The SLOT values for sulphuric acid mist are derived in *Toxicology of Substances in Relation to Major Hazards: Sulphuric Acid Mist* (R.M. Turner and Fairhurst, 1992).

Sulphuric Acid mist is an irritant which has two main effects. One is constriction of the airways (bronchioconstriction and possibly laryngeal spasm). The other is damage to the respiratory tract accompanied by oedema and haemorrhage. These toxic effects depend on the size of the droplets.

Sulphuric acid mist is formed from releases of sulphur trioxide or oleum, a mixture of sulphuric acid and sulphur trioxide. On release these react with water in the atmosphere and form a dense cloud of mist. The mist is likely to contain submicron droplets which remain airborne until they absorb additional water and rain out or are deposited onto surfaces. In an accident, the size of the droplets inhaled can be expected to exceed that on release and the authors assume a droplet size of 1 μm. As it happens, this is the size for which most of the data are available.

For sulphuric acid mist the bulk of data on animal experiments relates to guinea-pigs. This is also the most sensitive species. From the work of Amdur, Schulz and Drinker (1952) the authors obtain an estimate of the LC_{50} of 60 mg/m^3 for a 60 minutes exposure. For the index n Turner and Fairhurst use the values of the LC_{50} at an 8 hour exposure of 18, 30 and 50 mg/m^3 reported by Amdur, Schulz and Drinker and by Wolff *et al.* (1979), and obtain the value $n = 2$. These data form the basis of the SLOTs. There is no explicit recourse to LC_{05} or LC_{01} values, but the LC_{50} is that for the experiments in which the animals were most sensitive; in other work by Treon *et al.* (1950) and Amdur (1958) no deaths were recorded at concentrations up to 42 and 121 mg/m^3 for an exposure time of 60 minutes. The resultant SLOTs and DTL equation are then as given in Table 18.29.

18.22 Gas Toxicity: Combustion Gases

A somewhat separate problem concerns the toxicity of combustion products. Much of the research interest in such gases centres on the combustion of furnishings, but work in this area is also relevant to toxic clouds from combustion of materials on plant and in storage, particularly warehouses.

Work on the toxicity of combustion products has been described in a number of publications. This includes work described in *Smoke and Products of Combustion* (Hilado, 1973) and by Hilado and co-workers (Hilado and Furst, 1976; Hilado, Casey and Furst, 1977; Hilado, Cumming and Casey, 1978; Hilado and Cumming, 1978; Hilado and Huttlinger, 1980, 1981b,c), Hartzell and co-workers (Kaplan and Hartzell, 1984; Hartzell, Packham *et al.*, 1985; Hartzell, Priest and Switzer, 1985; Hartzell, Stacy *et al.*, 1985; Hartzell, 1987, 1989; Hartzell, Grand and Switzer, 1987), Underwood (1978), Alexeeff *et al.* (1986), Tsuchiya and Nayaka (1986) and the CPD (1992b).

The toxicity of combustion products in the context of hazard assessment has been considered by D.A. Carter

(1989), G.T. Atkinson, Jagger and Kirk (1992) and G.T. Atkinson and Jagger (1994). The toxicity of the breakdown products of the fire extinguishant bromochlordifluoromethane (BCF) has been studied by Doe *et al.* (1986)

18.23 Ultratoxic Substances

The Seveso disaster in 1976 showed that there is a serious hazard from small quantities of ultratoxic substances. At Seveso some 2.5 kg of 2,3,7,8–tetrachlorodibenzo-paradioxin (TCDD) were released to the atmosphere. Abnormal reaction conditions occurred in a chemical reactor, the pressure rose and the relief valve operated. The TCDD was not a normal reaction product but the product of a side reaction which occurred at an appreciable rate only under abnormal conditions. The toxicity of TCDD is such that it is more akin to a chemical warfare agent than an industrial chemical and it has been called the most poisonous substance in existence. The surrounding area was contaminated and had to be evacuated. People in the area at the time of the incident suffered rashes. But, more seriously, there were expected to be long-term carcinogenic, teratogenic and/or mutagenic effects. Further details of the Seveso incident are given in Appendix 3.

A further disaster involving a very highly toxic, if not ultratoxic, chemical occurred at Bhopal in 1984, where a reaction occurred in a storage tank containing methyl isocyanate (MIC), the relief valve lifted and released a cloud of the gas onto housing, killing a large number of people, the official death toll being now 4000, but other estimates being rather higher. This was much the worst accident experienced at a chemical plant. Further details of the Bhopal incident are given in Appendix 5.

18.24 Plant Design for Toxic Substances

Plants handling toxic substances need to be designed to minimize both large accidental releases and fugitive emissions. An overview of the design of plant for the handling of toxic substances is given by S.D. Green (1980). He deals with: the collection and assessment of toxicological information; process reviews covering random leaks and intermittent releases; design strategies of substitution, prevention and containment; ventilation; separation distances; and protection measures.

18.24.1 Design against large releases

As far as concerns large toxic releases, this is not solely a matter of the mechanical design of the plant, important though that is. Inherently safer design also has an important part to play, in minimizing the effects of any failure through the choice of the substances used in the in process and the operating conditions.

The mechanical design of plants, and particularly pressure systems, to high standards of integrity is treated in Chapter 12, and is not considered further here.

18.24.2 Design against fugitive emissions

There are a number of accounts, both by plant designers and occupational hygienists, of the design and operation of plant handling toxic substances to counter fugitive emissions and the resultant chronic toxic hazard. These include *Fugitive Emissions of Vapours from Process Equipment* (Jones *et al.*, 1984, BOHS TG3), (the BOHS *Fugitive Emissions Guide*) *Health Hazard Control in the Chemical Process Industry* (Lipton and Lynch, 1987) and *Handbook of Health Hazard Control in the Chemical Process Industry* (Lipton and Lynch, 1994) and by Payne (1978), S.D. Green (1980), Kusnetz and Phillips (1983), Kusnetz and Lynch (1984), Whitehead (1987) and Crowl and Louvar (1990).

Other potential sources of guidance are design practices for chemical plant under vacuum and for nuclear plant.

Emissions of toxic substances to the atmosphere are not confined to continuous leaks from the plant. They also occur as a result of operations carried out on the plant, particularly those involving purging or breaking into equipment for operations or maintenance purposes. The design of plants to minimize exposure to toxic substances is essentially a two-pronged one, based on the reduction of fugitive emissions and the provision of ventilation.

The problem of fugitive emissions on process plants is discussed in Chapter 15. There has been a growing concern over the emission of hydrocarbons and of volatile organic compounds (VOCs). Two points made there bear reiteration. One is that there is considerable variability between plants in the levels of emission, and the other that it is possible for plants to achieve very low levels of emissions, though as always this is easier in the design of a new plant.

Most of the data on fugitive emissions relate to hydrocarbons and VOCs. They provide a useful initial indication, but in view of the wide differences in the results obtained and the rather different nature of the problem in the case of toxic materials, care should be exercised in applying them to toxic emissions.

The BOHS *Fugitive Emissions Guide* provides guidance on the main leak sources: flanges and seals, with applications of the latter on valves, agitators, pumps and compressors.

The topics treated by Lipton and Lynch (1987) are (1) occupational health hazards, (2) sources of exposure, (3) exposure evaluation, (4) fugitive emissions, (5) hazard control, (6) rotating equipment, (7) valves and flanges, (8) sampling, and (9) drains, sewers and wastewater emissions.

18.24.3 Ventilation

Design to minimize fugitive emissions is complemented by provision of good ventilation. Ventilation is discussed in Chapter 10 in relation to plant layout, and again in Chapter 25 in relation to occupational hygiene, and is therefore not treated at this point.

18.24.4 Material transfer

On plants handling toxic materials, transfer systems such as pumps are one of the main sources of emissions, which can occur either as random leaks or in the course of activities such as maintenance. An account of this problem and measures to deal with it has been given by Grossel (1990a).

This author considers centrifugal pumps, positive displacement pumps, sealless pumps, jet pumps, pressurized gas and vacuum systems. He describes centrifugal pumps for toxic-liquids which are fitted with double

mechanical seals, in double inside or tandem arrangement, and with a seal failure alarm. A buffer liquid may be used, which may have to be cooled to remove heat or heated to reduce its viscosity. A minimum flow bypass is often desirable and may need to be provided with a cooler. For a heat sensitive toxic liquid it may be necessary to provide the pump with a high temperature trip.

For low flows, positive displacement pumps are frequently used. Diaphragm metering pumps or air-operated diaphragm pumps have no seals and are able to operate at low flow without excessive temperature rise. For highly toxic liquids, Grossel advises double diaphragm pumps. The space between diaphragms can be monitored. For rather higher flows use may be made of rotating positive displacement pumps such as the gear, vane, lobe or screw types, fitted with double mechanical seals or using magnetic drives. Positive displacement pumps require pressure relief to an external source. Grossel emphasizes the need for such external relief even where the pump is equipped with an internal relief valve.

Sealless pumps such as canned pumps and magnetic drive pumps are another option, but these also are not without problems. One weak point may be the shell, which may be relatively thin so as not to impede the magnetic field. Another may be the bearings which are lubricated by the pumped fluid. Failure of a bearing can cause the rotor to rub against the can and rupture it. Manufacturers offer various arrangements to overcome these problems, such as secondary containment with monitoring of the intervening space or monitoring of the bearings. Operating problems include flashing of low-boiling liquids, dry running and blockage by solids.

Grossel also gives details of systems for transfer by pressurized gas or by vacuum, and discuss other aspects such as plant layout, equipment installation, remotely operated isolation valves and ventilation hoods.

18.25 Toxic Gas Detection

A release of toxic gas may be detected by the visual appearance of the cloud, by its odour or by instrumentation. Detection by these means is discussed in the *Vapor Release Mitigation Guidelines* (CCPS, 1988/3).

18.25.1 Colour

Some gases have a characteristic colour. Chlorine gives a gas cloud of greenish-yellow colour, bromine one of reddish-orange colour, and so on. Even if there is no such colour, the gas may well form a visible fog. Some gases tend to form a fog by taking up moisture from the air to form an aerosol. Such gases include ammonia, hydrogen chloride, hydrogen fluoride and sulphur trioxide. Liquefied gases such as Liquefied natural gas (LNG), liquefied petroleum gas (LPG), liquid ethylene and liquid ammonia cause water in the atmosphere to condense and create a fog.

18.25.2 Odour

Many gases give a characteristic odour. The concentrations at which such an odour is detectable vary by orders of magnitude.

Accounts of odour are given in *Human Responses to Environmental Odors* (Turk, Johnston and Moulton, 1974), *Industrial Odor Technology and Assessment* (Cheremisinoff and Young, 1975), *The Identification and Measurement of Refinery Odours* (CONCAWE, 1975 8/75), *Compilation of Odor and Taste Threshold Values Data* (Fazzalari, 1978), *The Perception of Odors* (Eugen, 1982) and *Odor Thresholds for Chemicals with Established Occupational Standards* (AIHA, 1989/17), and by Leonardos, Kendall and Barnard (1969), Amoore and Hautala (1983), Polak (1983), Lynskey (1984 LPB 60) and J.C. Stevens, Cain and Weinstein (1987). Odours are also discussed in Appendix 11.

Some odour thresholds are very low indeed. The threshold for hydrogen sulphide is given in the CONCAWE document as 0.001–0.014 ppm and in the CCPS *Guidelines* as 0.0002 ppm. The latter give data on the relation between the odour threshold (OT) and the immediately dangerous to life and health (IDLH) limit. These include the following:

Gas	*OT* (ppm)	*IDLH* (ppm)	*IDLH/OT*
Carbon monoxide	(none)	1500	N/A
Phosgene	0.47	2	4.3
Ammonia	21	500	25
Chlorine	0.31	25	80
Hydrogen sulphide	0.0002	300	1 500 000

In some cases a person can become desensitized to an odour. The classic case is hydrogen sulphide. This is discussed in Section 18.16.

18.25.3 Instrumentation

In some cases it is appropriate to install toxic gas detectors. Accounts of toxic gas detectors and detection are given in *Detection and Measurement of Hazardous Gases* (Cullis and Firth, 1981) and by Dailey (1976), Johanson (1976), Warncke (1977), Lichtenberg and McKerlie (1979), Harbert (1983, 1984), Krigman (1984), Zanetti (1986b) and Atallah and Guzman (1987).

Whereas much flammable gas detection is based on combustible gas detectors, toxic gas detection tends to utilize a wider variety of detectors, corresponding to the variety of toxic gases. Some principles of operation in the sensors used include (1) hot wire combustion, (2) catalytic combustion or reaction, (3) some other chemical reaction, (4) electrical effects, and (5) absorption and scattering effects. Use is also be made of closed circuit TV monitors. Details of sensors and their response times are given in the CCPS *Guidelines*.

The purpose of a toxic gas detection system should be clearly defined. One purpose may be to give a rapid warning of a major release. Another may be to detect fugitive emissions of a toxic gas for occupational hygiene purposes. It is the former which is considered at this point.

In locating the detectors there is a choice between monitoring specific potential leak sources and giving good area coverage. For the monitoring of a leak source Johanson (1976) suggests an angular separation between detectors of 10° and a separation between detectors of no more than 30 ft (10 m). He recommends detector heights of 1.5 ft (0.5 m) and of 6–8 ft (2–2.5 m) for buoyant gases.

The *CCPS Guidelines* emphasize that a toxic gas detection system with an insufficient number of detectors or inadequate maintenance may be worse than no system at all, particularly if it leads to less human surveillance or to confusion arising because a field report of a leak is not confirmed by the detection system.

Guidance is available on gas detection systems for specific toxic gases. For chlorine information is given in the *Chlorine Manual* (Chlorine Institute, 1986 Pmphlt 1). The monitoring of ammonia is discussed by Lichtenberg and McKerlie (1979).

18.26 Toxic Release Response

Essentially the control of the toxic release hazard means, on the one hand, the prevention of serious loss of containment and, on the other, the elimination of hazardous concentrations in the environment. There are also the intermediate problems of dealing with small quantities of toxic materials arising mainly from leaks and spillages and from maintenance operations.

Aspects of the process and plant design and of the storage and transport of toxic chemicals are described in Chapters 11, 12, 22 and 23, respectively. Another aspect is planning for toxic emergencies, which is described in Chapter 24. The assessment of the hazard of large toxic releases is dealt with in Sections 18.28–31.

Elimination of hazardous concentrations in the working environment requires assessment of leaks and other sources of toxic substances. Engineering measures can then be taken to improve the leak-tightness of plant.

It is also necessary to have ventilation and monitoring of the atmosphere and medical checks on personnel. These latter aspects comprise industrial hygiene and are discussed in Chapter 25.

In addition, there should be procedures for the handling of abnormal leaks and spillages.

18.26.1 Leaks and spillages

If the plant is in the open, small leakages from the plant may be dispersed by the wind. If the plant is in a building, mechanical ventilation is necessary. The toxic hazard should be a principal consideration in deciding whether to put a plant in a building or in the open.

Provision should be made for handling larger emissions. It may be necessary to have emergency isolation valves and relief, blowdown and gas absorption facilities in order to reduce the amount likely to escape.

Methods of dealing with liquid spillages vary with the chemical concerned. Thus, for example, the treatments recommended in the respective codes are different for chlorine and for phosgene. In both cases the principle applies of restricting by containment the area available for evaporation. But, whereas the evaporation of chlorine can be reduced by applying mechanically produced water-based protein foam, this should not be utilized for phosgene, for which the use of kerosene impregnated with dry sawdust is suggested.

In dealing with spillages, actions should be avoided which actually increase the rate of evaporation. For example, water should not be sprayed on a chlorine spillage. In contrast, a spillage of ethylene oxide, which is miscible with water, may be diluted and rendered more safe by the addition of large quantities of water. Restricted amounts of water, however, may only serve to increase the vaporization.

The handling of toxic liquids spilled into bunds, and the use of foams, is considered in more detail in Chapter 15.

18.26.2 Emergency action

The effect of a large toxic release can be greatly mitigated if the people exposed take the right action. In plant handling toxic materials workers have protective buildings and equipment and are trained in emergency procedures. It is commonly considered that, provided these precautions are taken, workers in the factory itself are at no more risk than members of the public.

In order to prepare instructions to be issued to the public in the event of a large release, it is necessary to decide whether it is safer for a person to flee from the gas cloud or to stay indoors taking measures to prevent ingress of the chemical. Methods are available for the calculation of the rate at which a toxic gas diffuses into buildings. An account of these methods was given in Chapter 15.

The usual practice in assessing a toxic release hazard is to consider a range of scenarios. For some scenarios the best course of action may be to evacuate, while for others it may be to stay indoors. It should be borne in mind, however, that any instruction to be issued to the public should be simple and clear. In most cases the preferred advice to the public is to stay indoors and shut doors and windows.

Emergency procedures for toxic releases are treated in more detail in Chapters 20 and 24.

18.27 Toxic Release Case Histories

By far the worst accident in the history of the process industries occurred on 3 December 1984 at Bhopal, where water entered a storage tank of methyl isocyanate, causing overheating and release of methyl isocyanate vapour which spread over a shanty town close to the works and killed some 4000 people. This incident is described in Appendix 5.

There have been a number of major accidents involving chlorine. A list of major chlorine accidents world-wide has been given by Simmons, Erdmann and Naft (1974) and is reproduced in Table 18.30. Another list of chlorine accidents has been given by V.C. Marshall (1977b) and is shown in Table 18.31.

In 1939, failure of a chlorine storage tank at Zarnesti, Romania, resulted in the death of about 60 people. This is the largest death toll from any industrial chlorine accident.

As the tables show, tank failures were also the cause of two other major chlorine accidents: at St Auban, France, in 1926, for which the death toll is given variously as 19 and 40; and at Rauma, Finland, in 1947, where 19 died.

An explosion in a rail tank car at Mjodalen on 26 January 1940 resulted in a chlorine release of 7–8 te and caused the gassing of 85 people, of whom three died (Römcke and Evensen, 1940; Hoveid, 1966).

A large release of chlorine occurred at Baton Rouge, Louisiana, on 10 December 1976 (Case History A79), which the *Second Report* of the ACMH (Harvey, 1979b) described at the time as believed to be the largest civil

Table 18.30 *Significant chlorine accidents (after Simmons, Erdmann and Naft, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Date	*Location*	*Chlorine release* (ton)	*Fatalities*	*Comments*
Storage tanks				
1926 Dec. 13	St. Auban, France	25	19	Tank burst
1929 May 10	Syracuse, NY	25	1	Tank burst, H_2–Cl_2 explosion
1939 Dec. 24	Zarnesti, Roumania	25	*c.* 60	Tank burst
1947 Nov. 5	Rauma, Finland	30	19	Tank burst from overfilling
1952 Apr. 4	Wilsum, Germany	15	7	Tank failed (a converted old boiler)
Barges				
1960 Apr. 13	–		1	Loading hose ruptured
1961 Feb. 23	–	0		Wychem 112 sinking, no leak
1965 Sep. 12	Nr. Baton Rouge, LA	0		Sunk during Hurricane Betsy, no leak
1970 Jul. 28	–		1	Unloading pump break
1972 Mar. 19	Nr. Louisville, KY	0		Broke from tow and rested on dam, no leak
Rail tank cars				
1934 Feb. 28	Niagara Falls, NY	16		Anchor failure
1935 Mar. 13	Griffith, IN	30		Anchor failure
1947 Feb. 4	Chicago, IL	18		Release caused by heat from fire
1961 Jan. 31	La Barre, LA	30	1(114 'gassed')	Train wreck, tank punctured
1962 Nov. 30	Cornwall, Ont.	30	(89 gassed)	Anchor failure
1963 Apr. 28	Brandtsville, PA	9		Valves sheared off in wreck
1963 Aug. 9	Philadelphia, PA		(430+ gassed)	Loading line broken when tank was rammed
1967 Nov. 8	Newton, AL	55		Tank punctured in wreck
Truck tanks				
No significant accidents				
1-ton containers				
1928 Jul. 7	Asbokan, NY			Exploded, contamination with NCl_3
1928 Jul. 13	Asbokan, NY			Exploded, contamination with NCl_3
1969 May 8	Cleveland, OH		2	–
Pipelines				
1936 Nov. 12	Johnsonburg, PA	3	1	Transfer line broken by housing
1949 Sep. 1	Freeport, TX	5		8 in. line burned in attempted welding
1964 Jul. 12	Mobile, AL		1	–
Cylinders				
1920	Niagara Falls, NY		3	150 lb cylinder burst
1925	De Noya, OK	1	Suckback of gasoline	
1947 Jan. 13	Natrium, VA		2	150 lb cylinder exploded
1954 Jun. 25	Montreal, Quebec		1	Cylinder fell into hold of steamship

chlorine release recorded. An explosion occurred which is thought to have dislodged a chlorine tank and caused it to fall on a protruding object and to puncture. Approximately 90 te of chlorine escaped, but there were no deaths.

Another smaller but more lethal chlorine release occurred from a derailed rail tank car at Youngstown, Florida, on 26 February, 1978 (Case History A94). Seven people were killed.

Another large release of chlorine occurred on 1 August 1981 when a train derailment near Montana, Mexico (Case History A100), resulted in the rupture of two 55 te chlorine tankers. The gas spread through a narrow valley and caused the deaths of 17 people.

A derailment of a chlorine train at La Barre, Louisiana, on 31 January 1961 (Case History A29) gave rise to a release of chlorine. There was a house occupied by a family only 50 yd from the crashed chlorine rail tank car. A child taken out of doors died, but an infant who remained in the house survived. The incident is of interest, therefore, in relation to the protection provided by buildings.

There have also been a number of non-fatal chlorine releases. The chlorine accidents at Cornwall, Ontario, in 1962, at Philadelphia, Pennsylvania, in 1963, and at Los Angeles, California, in 1966, resulted in the gassing, but not the deaths, of quite large numbers of people.

Table 18.31 *Some data on the relation between size of toxic release and number of fatalities (after V.C. Marshall, 1977b) (Courtesy of the Institution of Chemical Engineers)*

Date	*Location*	*Equipment*	*Material released* (t)	*Fatalities*	*Mortality index* (deaths/t)
Chlorine					
1947 Nov. 5	Rauma, Finland	Storage tank	30	19	0.63
1939 Dec. 24	Zarnesti, Roumania		25	*c*. 60	*c*. 2.40
1926 Dec. 13	St. Auban, France		25	40[a]	1.60
1929 May 10	Syracuse, NY		22.5	1	0.004
1952 Apr. 4	Wilsum, Germany		15	7	0.46
1917	Wyandotte, MI		13.6	1	0.073
1956 Mar. 10	Lake Charles, LA		2.7	0	0
1967 Nov. 8[b]	Newton, AL		50[c]	0	0
1935 Mar. 13	Griffith, IN	Rail tank car	27.5[c]	0	0
1961 Jan. 31	La Barre, LA		27.5[c]	1	0.036
1962 Nov. 30	Cornwall, Ont.		27.5[c]	0	0
1947 Feb. 4	Chicago, IL		16.3[c]	0	0
1973 Mar. 5	Loos, BC		15.5	0	0
1934 Feb. 28	Niagara Falls, NY		14.5[c]	0	0
1963 Apr. 28	Brandtsville, PA		8[c]	0	0
1940 Jan. 26	Mjodalen, Norway		8	3	0.375
1914?	Chrome, NJ		7	0	0
1966 Jun. 14	La Spezia, Italy		7	0	0
1957 Oct. 19	Runcorn, UK		2–3	0	0
1928 Jul. 7, 13	Asbokan, NY		2	0	0
1950 Jul. 20	Billingham, UK		0.5	0	0
1969 May 8[b]	Cleveland, OH	Two 1-ton containers	1	1	1
1961 Feb. 23	Billingham, UK	Pipeline	12	0	0
1949 Sep. 1[b]	Freeport, TX		5	0	0
1936 Nov. 12[b]	Johnsonburg, PA		3	1	0.33
1970 Oct. 19	Javle, Sweden		2	0	0
1920	Niagara Falls, NY	Cylinder	0.066	3	45
1947 Jan. 13	Natrium, WV		0.066	2	30
1925	De Noya, OK		0.066	2	30
1954 Jun. 25	Montreal, Canada		0.066	1	15
Total of 30 incidents			271	142	
Mean of 30 incidents			9.03	4.73	0.52
Ammonia					
1970 Nov. 16	Blair, NE	Storage tank	145	0?	0?
1973 Jul. 13	Potchefstroom, SA		38	18	0.71
1969 Feb. 18	Crete, NE	Rail tank car	64	6	0.094
1968 Aug. 21	Lievin, France		15?	5	0.33?
1971 Jun. 5	Floral, AR	Pipeline	570	0	0
1973 Dec. 6	Kansas City,[d] KS		210	0	0
Total of 6 incidents			1042	29	
Mean of 6 incidents			173	4.83	0.027
Phosgene					
1928 May 20	Hamburg, Germany	Storage tank	10?	10	1.0?

[a] This value differs from that given by Simmons, Erdmann and Naft (1974).
[b] The date quoted in the original reference has been corrected (F.P.L.).
[c] This value is about 10% less than that given by Simmons, Erdmann and Naft (1974).
[d] This incident is referred to elsewhere in this book as McPherson, Kansas.

Three chlorine releases from pipelines at Dominguez, California, in 1966 and 1967, are recorded by Solomon, Rubin and Okrent (1976). In each instance the amount of chlorine released was 500 lb. In one case the pipe was accidentally cut by a welder, in the other two it was accidentally dug up.

The release of 100 lb of chlorine from a cylinder into the subway system of Brooklyn, New York, in 1944, which is described by Chasis *et al.* (1947), resulted in the gassing, but not the deaths, of 208 people. It illustrates the effect of an escape in a confined space.

Another chemical which presents a serious toxic release hazard is ammonia. A list of ammonia accidents has been given by V.C. Marshall (1977b), as shown in Table 18.31.

A road tanker crash which released ammonia at Lieven, France, in 1968 resulted in 5 deaths (Medard, 1970), and an ammonia release from a crashed rail tank car at Crete, Nebraska, in 1969 killed 8 people.

There was a release of 160 ton of ammonia from a storage tank at Blair, Nebraska, in 1970 (Case History A47), but there were no casualties.

The ammonia accident at Potchefstroom, South Africa, on 13 July 1973 (Case History A65), in which 18 people were killed when an ammonia storage tank failed and released an estimated 39 ton, appears to be the worst accident involving ammonia for which details are available.

In 1976, a road tanker crashed on the Southwest Freeway, Houston, Texas (Case History A84), and released 19 te of ammonia which killed six people.

An ammonia release at Cartegena, Columbia, in 1977, is reported to have caused a death toll which is now set at 21 (MHAP, 1988). This is the largest number of deaths from an industrial ammonia accident.

On 20 March 1989 a refrigerated atmospheric ammonia storage tank containing some 7000 te of liquid ammonia failed at Jonova, Lithuania (Case History 128). The ammonia ignited and an ammonium nitrate storage caught fire. It is estimated that some 1400 te of ammonia evaporated and that a further 700 te of ammonia and nitrous fumes participated in the toxic fire plume. The plume is described as spreading some 35 km and affecting an area of some 400 km^2. Seven people were killed.

There have also been a number of non-fatal releases of ammonia. A release of about 600 ton of ammonia occurred from a pipeline in Floral, Arkansas, in 1971 (Chementator, 1971 Jul. 26, 55). There was a fish kill, but no injuries. There was an escape of some 230 ton of ammonia on a pipeline at McPherson, Kansas (Case History A64), in 1973.

Further incidents involving ammonia release are related by Slot (1938), Caplin (1941) and Trotter (1983). Other accounts are referenced by Payne, Delic and Turner (1990).

In general, the recorded releases of ammonia usually involve larger quantities than those of chlorine, but are not more lethal. As Table 18.31 shows, there are a number of recorded ammonia releases in excess of 100 te.

The toxicity of ammonia is appreciably less than that of chlorine and, although it behaves on release as a heavy gas, it has a molecular weight (MW 17), less than that of air, which eventually aids dispersion.

Some other major toxic release accidents include those tabulated below:

Date	*Location*	*Chemical*	*Deaths/injuries*
1928	Hamburg, Germany	Phosgene	10 d
1930	Lüttich, Belgium	Hydrogen fluoride, sulphur dioxide	63 d
1950	Poza Rica, Mexico	Hydrogen sulphide	22 d, 320 i
1978	Chicago, IL	Hydrogen sulphide	8 d, 29 i

The phosgene release in Hamburg in 1928 (Case History A6) was due to a pressure vessel failure. It caused the gassing of some 300 people and resulted in 10 deaths.

A gassing incident involving hydrogen sulphide at Poza Rica, Mexico, in 1950, is described by McCabe and Clayton (1952). There are numerous accounts of lesser hydrogen sulphide gassing incidents, including those by Haldane (1896), Poda (1966) and Burnett *et al.* (1977). Other accounts are referenced by R.M. Turner and Fairhurst (1990).

There have also been several fire incidents, described by the MHAP (1993), in which significant quantities of phosgene are said to have been generated. More generally, large fires are a source of toxic products. A fire in a fertilizer warehouse at Nantes in 1987 led to the evacuation of some 40 000 people (Pietersen, 1988b). The decision to evacuate was made on the basis of one measurement, taken inside a car, and may well have been unnecessary.

A even larger evacuation was that at Mississauga, Toronto, in 1979 (Case History 97), when a holed chlorine rail tank car led to an extended emergency in which some 215 000 people were evacuated. This incident is also described in Chapter 24.

Another major evacuation occurred at Glendora, Mississippi, in 1969 (Case History A43), where a ruptured rail tank car of vinyl chloride monomer caused some 30 000 people to be evacuated.

In some cases the material release is flammable as well as toxic. The ignition of the ammonia release at Jonova has already been described. Another case where a toxic release was ignited occurred at Nuremburg in 1980, when vinyl chloride issuing from a large hole in a derailed rail tank car found a source of ignition within seconds (Ernst, 1983).

Another type of toxic incident is the release of an ultratoxic substance, such as TCDD. Case histories involving TCDD are given in Appendix 3 on Seveso in 1976.

18.28 Toxic Release Risk

18.28.1 Historical experience

Only a small proportion of the major accidents listed in the loss prevention literature are toxic releases. Many toxic releases disperse rapidly, causing relatively few casualties.

In general, for all three major hazards – fire, explosion and toxic release – the large number of fatalities given by some theoretical estimates, assuming the most unfavourable and improbable circumstances and using models which may prove to be based on pessimistic assumptions, has been in contrast with the small number of fatalities shown by the historical record. Until 1984, this discrepancy was particularly striking for toxic releases. However, in that year the disaster at Bhopal demonstrated that, very rarely, an event occurs which gives some credence to the more pessimistic estimates.

Of the incidents described in Section 18.27, the worst accidents for particular major industrial toxic gases have been:

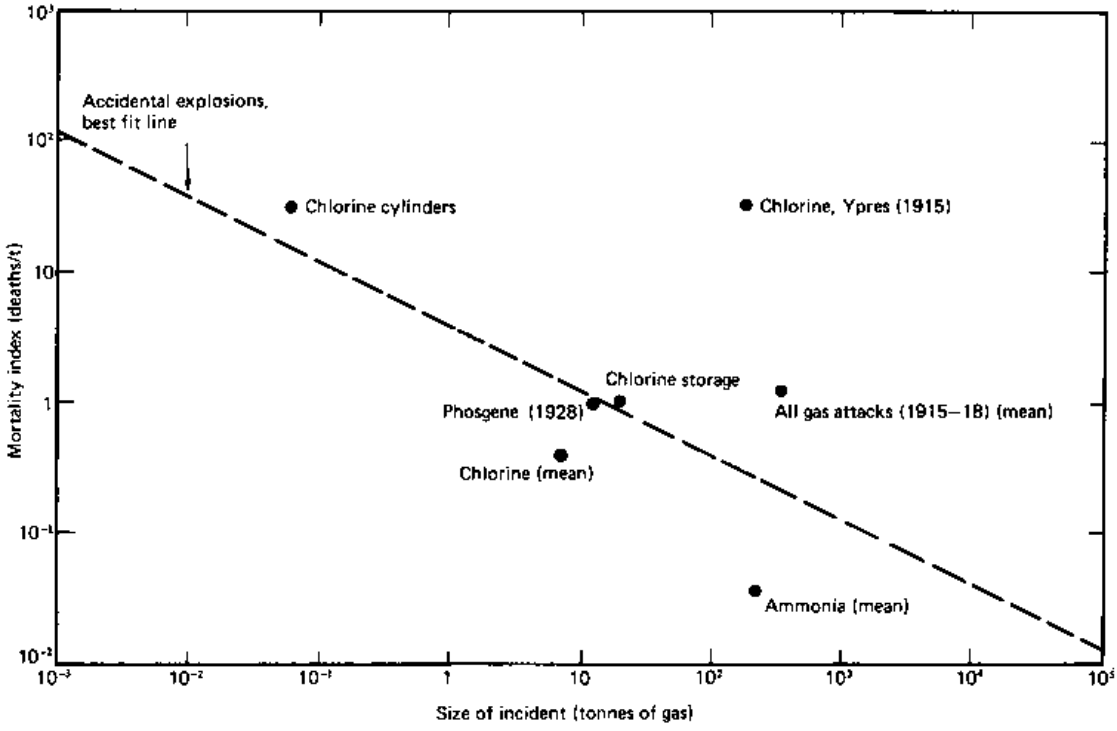

Figure 18.10 *Mortality index for toxic releases (after V.C. Marshall, 1977b) (Courtesy of the Institution of Chemical Engineers)*

		No. of deaths
Bhopal	Methyl isocyanate	*c.* 4000
Lüttich	Hydrogen fluoride, sulphur dioxide	63
Zarnesti	Chlorine	60
Poza Rica	Hydrogen sulphide	22
Cartegena	Ammonia	21
Hamburg	Phosgene	10

Prior to Bhopal, the most serious toxic incidents involved mainly chlorine and or ammonia.

Analysis of chlorine incidents has indicated that, with one exception, fatalities occur within about 400 m of the release, and generally within 250 m (MHAP, 1987).

In the UK there have been very few fatal accidents in chlorine factories and, as far as is known, none to the public, if such accidents as those arising from misuse of chemicals such as sodium hypochlorite are excluded.

The relation between the size of toxic release and the number of people killed has been investigated by V.C. Marshall (1977b), who has developed a mortality index (deaths/te) for toxic releases similar to that for explosions described in Chapter 17.

The list of toxic accidents given by V.C. Marshall (1977b), which is similar to but not identical with that given by Simmons, Erdmann and Naft (1974) and which also includes ammonia and phosgene accidents, has been given in Table 18.31. The table shows the number of fatalities and the mortality index.

In addition to the overall mortality index for chlorine, which is given in Table 18.31 as 0.52, the mortality index for chlorine storage tanks is also of interest. The value obtained for this from the incidents listed in Table 18.31 is 0.96.

Some values of the mortality index from the table are plotted in Figure 18.10. This figure may be compared with Figure 17.133, which gives a mortality index for explosions; the broken line in Figure 18.10 is that given for explosions in Figure 17.133.

Of these industrial releases those from cylinders tend to have a high mortality index. The amount of gas released is generally small, but the release probably often occurs in a building. A few deaths from such a release are sufficient to give a high value of the index.

It should be emphasized, however, that whereas in the case of explosions there is a well established relationship between the quantity of material and the explosion overpressure from which lethal effects can be estimated, there is at present no such relation for toxic releases.

18.28.2 Hazard assessment

The alternative approach to the determination of the risk from a large toxic release is the use of hazard assessment involving assumed scenarios of release and

with appropriate estimates of emission, dispersion and toxic effects. The hazard assessment may be generic or may address a particular situation, whether at a fixed site or in transport.

The largest number of hazard assessment studies has been done for chlorine. A large chlorine release has generally been regarded as one of the most serious hazards. The following account deals principally with chlorine, but some mention is made of other toxic substances, notably the other main toxic gas, ammonia.

Some early generic studies were those by Howerton (n.d., 1969) and Simmons, Erdmann and Naft (1974) on chlorine; Eisenberg, Lynch and Breeding (1975) on the vulnerability model on chlorine and ammonia; and Solomon, Rubin and Okrent (1976) on a variety of chemicals.

These studies had a number of features which would now be regarded as inappropriate. They generally made very pessimistic assumptions, as the authors emphasize. Two points may be noted in particular. Some of the release rates assumed are extraordinarily high, and in most cases no credit is given for mitigation. In addition, the studies used passive gas dispersion models.

Studies were also made for specific situations. These include a study of chlorine releases from a factory by Dicken (1974, 1975) and Sellers (1976) and a study of the modes of transport for chlorine by Westbrook (1974).

The next stage in hazard assessment of toxic releases is exemplified by the two *Canvey Reports* (HSE, 1978b, 1981a) and the *Rijnmond Report* (Rijnmond Public Authority, 1982). The *Canvey Reports* gave hazard assessments for ammonia and hydrogen fluoride, and the *Rijnmond Report* for acrylonitrile, ammonia, chlorine, and hydrogen sulphide, from a hydrodesulphurizer. These reports are described in Appendices 7 and 8, respectively. These studies are characterized by a more detailed treatment of the emission scenarios and flows, the use of heavy gas dispersion models and, to some extent, an allowance for mitigating factors. Subsequent work on the hazard assessment of toxic releases has generally retained the basic approach, but has significantly refined the methodology.

A further stage is the hazard assessment of toxic gases is the work described in the ACDS *Transport Hazards Report* (1991), which covers chlorine and ammonia and which is described in Chapter 23 and Appendix 17.

Accounts are given in Sections 18.29 and 18.30 of some of the hazard assessments just mentioned and in Section 18.31 of developments in the methodology. These should be taken in conjunction with the accounts in the *Canvey Reports*, the *Rijnmond Report* and the ACDS *Transport Hazards Report*.

18.29 Chlorine Hazard Assessment

18.29.1 Fixed installations

A major study of the assessment and control of the hazard of chlorine release from a large chlorine factory in the UK has been described by Dicken (1974, 1975), Sellers (1976) and Hewitt (1976). The chlorine factory concerned is shown in outline in Figure 18.11. It includes cellrooms, compression plant, liquefaction plant, gas absorption plant and distribution to user plants. The study falls into three parts: the development of risk criteria, the assessment of the hazards and the recommendations for improvements.

Four categories of hazard were defined. Category 0 involves no nuisance to the public, whereas Categories I–III do involve such a risk. Category I is the least serious

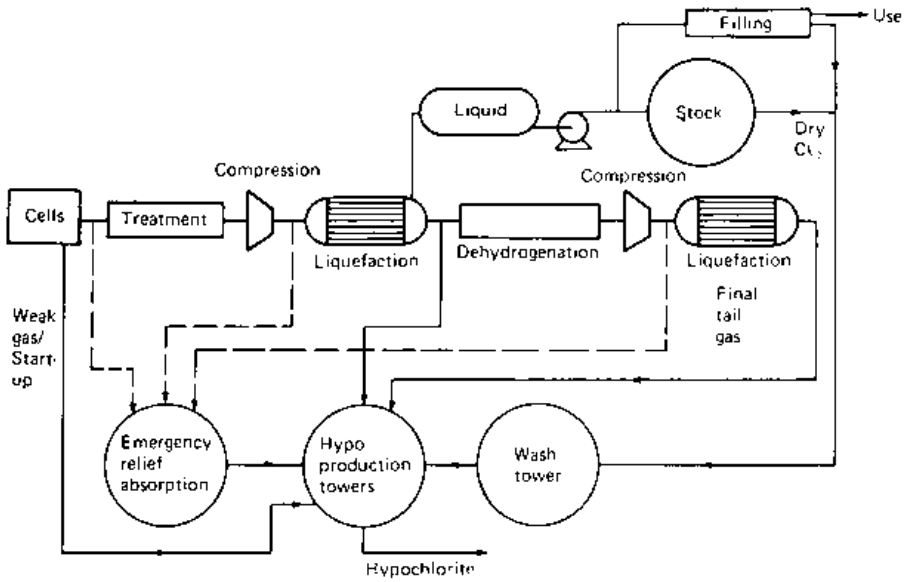

Figure 18.11 *Chlorine production, liquefaction and distribution system (Dicken, 1974) (Courtesy of the Electrochemical Society)*

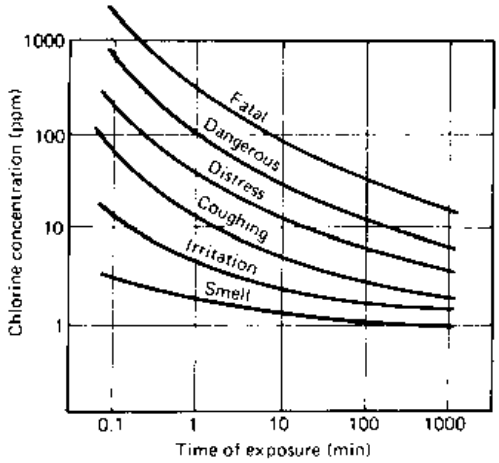

Figure 18.12 *Effects of exposure to different concentrations of chlorine vapour (Dicken, 1974) (Courtesy of the Electrochemical Society)*

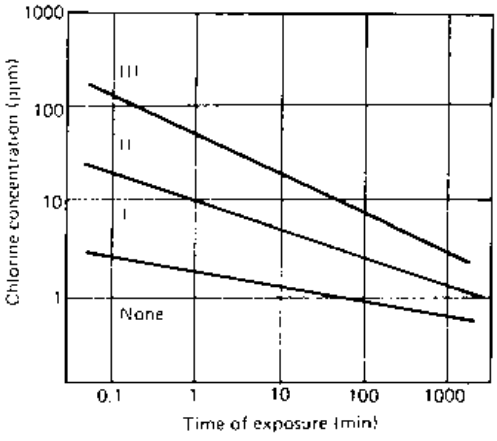

Figure 18.13 *Categories of chlorine release (Dicken, 1974) (Courtesy of the Electrochemical Society)*

and constitutes a nuisance to the public, but no more. Category II is a more severe release which could cause distress to people and damage to vegetation, and could give rise to claims for compensation. Category III is a major emission which, in addition, could result in injury or loss of life. The maximum frequencies suggested for events in Categories I and II were once in 1 and 10 years, respectively. A Category III release was considered acceptable once in 100 years, which was estimated to be roughly equivalent to a risk to the public of 10^{-7}/year per person.

Information on the toxicity of chlorine was studied and the relations between toxicity and exposure shown in Figure 18.12 were produced. The hazard categories were then defined more closely in terms of the toxic effects and the relations shown in Figure 18.13 were derived.

In assessing the effects of toxic substances, consideration needs to be given to members of the public who may be more susceptible than the average adult worker. Some relevant data quoted by Hewitt (1976) in this study were given in Table 9.22**.**

The historical data on chlorine releases throughout the works were also collected. These are shown in Table 18.32. Using these data as a guide, the works was divided into some 23 units and each unit was allocated a proportion of the target level of risk for the whole works. This allocation is shown in Table 18.33. Three two-man teams were then set up to study the 23 units, using in particular the hazard and operability study method.

With the situations leading to release thus identified, quantitative assessments were made of the frequency, size and effect of such releases. Estimates of frequency were based on reliability calculations and data, those on size on emission calculations, and those on effects on dispersion calculations, and toxicity data. These methods have been described in Chapters 7–9 and 15.

Extensive gas dispersion calculations were carried out using a specially developed computer program. The dispersion equation quoted is that formulated by Pasquill (1961) and used by Bryant (1964 UKAEA AHSB(RP) R42):

$$C = \frac{168QF}{\theta h d u} \qquad [18.29.1]$$

with

$$F = \exp(-2.303H^2/h^2) \qquad [18.29.2]$$

where C is the ground level concentration on the axis of the plume (m^3/m^3), d is the downwind distance (m), F is the stack correction factor, h is the vertical spread of the plume at distance d (m), H is the effective height of the stack (m), Q is the gas release rate (m^3/s), u is the wind speed (m/s); and θ is the lateral spread of the plume (°). The lateral spread θ and the vertical spread h are both functions of the atmospheric stability. Equation 18.29.1 is discussed in more detail in Chapter 15.

It is also stated that both instantaneous and continuous releases were studied. For a given emission point the investigation covered 18 wind directions, 6 wind speeds and 6 stability categories, making 648 permutations. Other factors taken into account were plume rise from the stack (where applicable), downwash from neighbouring buildings and multipoint sources such as ventilation ducts on the cellroom roof.

For a given emission situation and one permutation of weather conditions the maximum concentration at or outside the works boundary was computed and converted to a hazard of Category 0, I, II or III. From all the permutations the probabilities of hazards in the different categories were determined. Some examples of the results obtained are given in Table 18.34.

The validity of the assessment procedure was checked by comparison with historical data. Normally the ratio of the predicted to the observed frequency of release was in the range 1–2.

The study made recommendations for improvements both of hardware and of software, although not all proved practical. Some £1 m capital was spent, of

Table 18.32 *Chlorine releases at a major works in the UK – period 1966–70 (Dicken, 1974) (This table and Figures 18.11–18.13 were originally presented at the 145th Spring Meeting of the Electrochemical Society in San Francisco, CA, and are reproduced by permission of the author and of the Society)*

Source	(%)	*Prime cause*	(%)
Chlorine cellroom	15	Instrument/control failure	17
Dechlorination of brine	13	Human error	12
Hypochlorite tower	12	Machine failure	9
Tail gas treatment plant	11	Leaks	8
Drains	10	Maintenance/startup	6
Chlorinated organic plants	7	Service failure	5
Chlorine filling/loading	6	Miscellaneous	18
Cell gas treatment plant	6	Unknown/not recorded	25
Others	20		

Table 18.33 *Allocation of proportion of works chlorine releases between works units (Sellers, 1976) (Courtesy of the Institution of Chemical Engineers)*

	Percentage of works acceptable level
Major cellrooms	20
Emergency absorption plant	10
Compression and liquefaction plant	10
Small cellrooms	10
Liquid storage and pipelines	7
Container filling	4
Drum, cylinder and hypochlorite users	1
User plants (6 at 5% each)	30

which about a third was on the emergency absorption plant.

Hardware changes included the installation of additional equipment, such as stand-by power supplies or duplicate pumps, and of extra instrumentation. The availability of the equipment has sometimes been poor. Changes in software covered areas such as operating instructions and inspection and test methods. It is claimed that the work has resulted in a 40% reduction in the number of chlorine releases recorded in the areas covered and in an increase in plant availability.

Similar investigations have been carried out for other gases such as bromine, hydrogen chloride, hydrogen fluoride and phosgene. Another study in this area is the assessment of the hazard from acrylonitrile storage tanks described by Siccama (1973).

18.29.2 Transport

Howerton (n.d., 1969), in a generic study of the hazards of chlorine handling and transport, gives estimates of the areas affected by different chlorine releases based on calculations of (1) liquid and vapour discharges from containers, (2) flash-off and evaporation from liquid chlorine, and (3) dispersion from instantaneous and continuous point sources at ground level.

He considers both instantaneous and continuous releases and uses the Pasquill–Gifford equations. The equation used for a continuous point source is Equation 15.16.41 which gives the concentration profiles. The values of the dispersion coefficients used are those given by Singer and Smith (1966).

The scenarios considered are an instantaneous release of 25 000 lb and continuous releases of 1, 5 and 10 lb/s of chlorine in a 5 mile/h wind in both moderately stable and moderately unstable conditions. The dangerous chlorine concentration is taken as 35 ppm. Graphs are given showing the lines of constant chlorine concentration, or chlorine isopleths, for these eight cases. For the

Table 18.34 *Predicted chlorine releases and their consequences (Sellers, 1976) (Courtesy of the American Institute of Chemical Engineers)*

Incident	*Frequency* (events/year)	*Release rate* (m^3/h)	*Release duration* (min)	*Severity of event*					
				Percentage in class (%)			*Frequency of class* (events/year)		
				I	*II*	*III*	*I*	*II*	*III*
Cell offtake shut	0.7	70	5	30	2	0	0.21	0.014	0
Cell explosion	1.5	2	5	11	0	0	0.17	0	0
Control fails but relief operates	0.95	60	3	29	0	0	0.28	0	0
Control fails and relief fails	0.011	840	2	16	39	13	0.002	0.004	0.001
Total							0.7	0.02	0.001

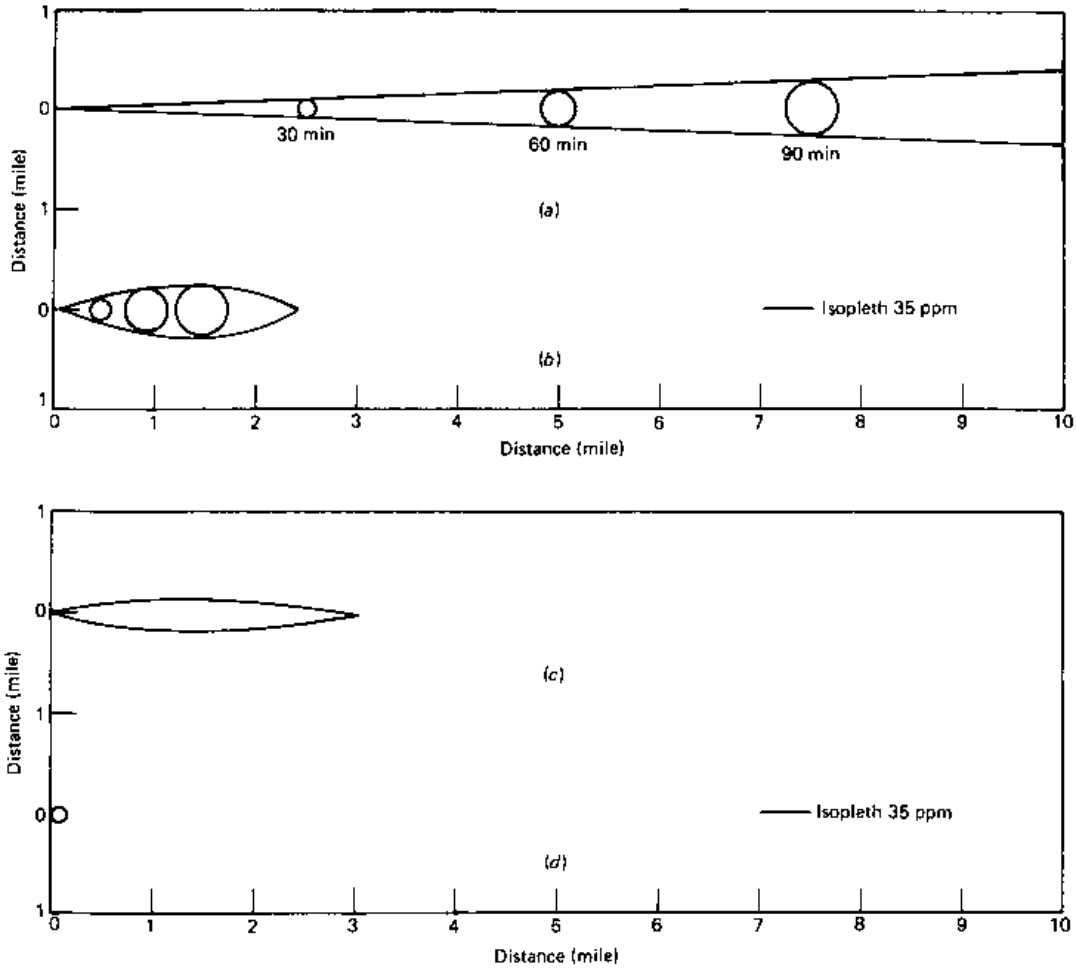

Figure 18.14 *Concentration profiles for chlorine releases from a point source at ground level (after Howerton, 1969): (a) instantaneous release of 25 000 lb in stable conditions; (b) instantaneous release of 25 000 lb in unstable conditions; (c) continuous release of 10 lb/s in stable conditions; (d) continuous release of 10 lb/s in unstable conditions (Courtesy of the American Institute of Chemical Engineers)*

instantaneous release the cloud is hemispherical in shape and travels with the speed of the wind. The cloud first expands in size and then contracts. But, whereas under stable conditions the cloud is continuing to expand even at a distance of 10 miles, under unstable conditions it starts to contract again after some $1\frac{1}{2}$ miles, as shown in Figures 18.14(a) and 18.14(b), respectively. In both cases the envelope of the area swept by the cloud is cigar shaped, but for stable conditions Figure 18.14.(a) shows only the expanding part of the envelope, while for unstable conditions Figure 18.14(b) shows the envelope terminating within about $2\frac{1}{2}$ miles. The time of passage of the cloud in stable conditions is quite short, about 5–15 minutes. For the continuous release of 10 lb/s the isopleth under stable conditions is approximately cigar shaped and reaches about 3 miles as shown in Figure 18.14(c), while under unstable conditions it is ovoidal and reaches only about $\frac{1}{8}$ mile as shown in Figure 18.14(d).

The conditions under which the highest gas concentration can occur at large distances are those of an instantaneous release under stable weather conditions at low (but not zero) wind speeds. In this sense, this is the worst scenario. In such a case, however, the cloud travels slowly and the warning time is long.

Simmons, Erdmann and Naft (1974) in another generic study of the hazards of chlorine transport have estimated the area affected by a chlorine release. They consider an instantaneous release and use the Pasquill–Gifford equations. The equation used is Equation 15.16.66a, which gives the dosage profiles. The values of the dispersion coefficient σ_y used are those given by D.B. Turner (1970). They are fitted to the following equation:

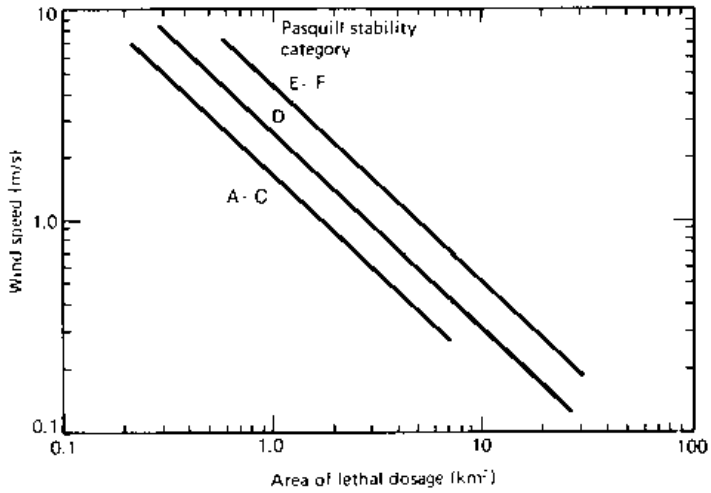

Figure 18.15 *Areas of lethal dose for initial flash vaporization from a 90 ton chlorine spill (Simmons, Erdmann and Naft, 1974) (Courtesy of the American Institute of Chemical Engineers)*

$$\sigma_y = kx^n \qquad [18.29.3]$$

with

	Pasquill category
$k = 0.20$	C
$k = 0.13$	D
$k = 0.078$	E, F
$n = 0.91$	

where x is the distance in the downwind direction (m), σ_y is the dispersion coefficient in the crosswind direction (m), k is a constant, and n an index. It is assumed that the dispersion coefficient σ_z is

$$\sigma_z = 0.2\sigma_y \qquad [18.29.4]$$

where σ_z is the dispersion coefficient in the vertical direction (m).

The relation between dosage and fatalities is taken to be as follows. For chlorine vapour in air

$$1 \text{ ppm} = 2.9 \text{ mg/m}^3 = 2.9 \times 10^{-6} \text{ kg/m}^3$$

The lethal dosage LCt_{50} is taken as

$$LCt_{50} = 1000 \text{ ppm min} = 0.17 \text{ kg s/m}^3$$

The scenario considered is the initial flash vaporization of 15.7 ton of chlorine from a spillage of 90 ton of chlorine, this being the capacity of a standard chlorine rail tank car. The area of lethal dosage LCt_{50} is a function of wind speed and stability conditions and may be represented by the equation

$$A = k'u^{-n'} \qquad [18.29.5]$$

where A is the area of lethal dosage (km^2), u is the wind speed (m/s), k' is a constant, and n' is an index.

For the case considered:

	Pasquill category
$k' = 1.72$	A–C
$k' = 2.83$	D
$k' = 4.92$	E, F
$n = 1.06$	

The areas of lethal dosage for this case are shown in Figure 18.15.

The conditions under which the area of lethal dosage from an instantaneous spillage is greatest are again those of release under stable weather conditions at low wind speeds. In this sense, this is again the worst case.

The authors compare their method of calculating the area of lethal dose with that of Howerton. For the 25 000 lb instantaneous release considered by Howerton the area of 4 km^2 calculated by him is greater by a factor of almost 4 than that obtained by their method. This is attributed to the use of different values of the dispersion coefficient.

The estimate of the area of lethal dosage is then used by Simmons, Erdmann and Naft in conjunction with data on the frequency of particular meteorological conditions and on population densities to calculate the potential fatalities for transport accidents, as described below. These are presented as histogram data for a range of accidents of increasing severity. The most severe accident calculated involved 5000–20 000 deaths with a frequency of 2.6×10^{-4}/year.

Table 18.35 *Effects of marine spillages of chlorine (after Eisenberg, Lynch and Breeding, 1975)*

Chlorine spillage (t)	*Stability condition*	*Wind speed* (m/s)	*Time of travel* (min)	*Distance travelled* (km)	*Fatalities*	*Injuries*
0.9	Neutral	4	10	2.4	277	645
	Unstable	5	8	2.4	0	0
	Neutral	4	30	7.2	277	5748
	Unstable	5	24	7.2	0	2
15	Neutral	4	10	2.4	921	0
	Unstable	4	10	2.4	921	0
	Unstable	5	8	2.4	0	921
	Neutral	4	30	7.2	9995	865
	Unstable	4	30	7.2	1020	6334
	Unstable	5	24	7.2	340	7425
1090	Neutral	4	10	2.4	921	0
	Unstable	5	8	2.4	1823	5734
	Neutral	4	30	7.2	13 628	937
	Unstable	5	24	7.2	18 152	4946

Eisenberg, Lynch and Breeding (1975) in the vulnerability model work already described have studied among other things the area affected by, and the lethality of, chlorine and ammonia releases.

They consider any instantaneous release from a marine spillage and use the Pasquill–Gifford equations. The equation used for an instantaneous release is Equation 15.16.40.

For chlorine the scenarios considered are instantaneous releases of 0.9, 15 and 1090 te of chlorine. The latter corresponds to the load of a large barge. The relation between dosage and fatalities is that given in the probit Equation 18.15.2**.** The populations at risk are defined in terms of the cell model already described.

Some results obtained are given in Table 18.35. These results indicate that the conditions under which the calculated lethality of the release is highest depend on the size of the release. For the small release of 0.9 te the lethality is higher under neutral conditions. With unstable conditions the gas is more rapidly diluted below its lethal concentration. For the large release of 1090 te the lethality is higher under unstable conditions. With unstable conditions the gas is more rapidly dispersed, but remains above its lethal concentration. The authors draw attention to the need to use short time steps in the calculation of $\Sigma C_i^n T_i$ in Equation 18.15.2 if accurate results are to be obtained.

For ammonia the scenarios considered are instantaneous releases of 8.2, 251 and 16 340 te. The relation between dosage and fatalities is that given by the probit Equation 18.15.3.

Some results obtained are as follows:

Ammonia spillage (t)	*Time of travel* (min)	*Distance travelled* (km)	*Fatalities*
8.2	Any	Any	0
251	10	2.4	921
	30	7.2	8 033
16 340	10	2.4	2 177
	30	7.2	18 151

The wind speed was 4 m/s. Toxic injuries were not assessed.

Major assessments of the hazard of chlorine transport have been described by Simmons, Erdmann and Naft (1974) and Westbrook (1974). Simmons, Erdmann and Naft have reviewed the methods used for the transport of chlorine in the USA, the historical experience of accidents involving chlorine and the hazards arising from its transport. They found that chlorine ranked sixth among chemicals in terms of the quantity produced. Some 4.4×10^6 ton of liquid chlorine were transported in 1972 and this amount was expected to rise to about 10×10^6 ton by 1990. Transport of chlorine is important, because accidents to carriers are relatively frequent, population densities along the main transport routes are relatively high, and the substance is very toxic.

The sizes of chlorine containers are basically as follows. Storage is typically in large pressure vessels or refrigerated atmospheric tanks containing 1000 or 2000 ton each. Barges usually carry four pressure vessels each containing 275 ton, making 1100 ton total capacity. Rail tank cars are pressure vessels ranging in size from 16 to 90 ton, but only the latter size is now made. Road tankers are also pressure vessels and normally have a capacity of 16 ton. Cylinder sizes are usually 1 ton, 150 lb or smaller.

All containers for chlorine transport are pressure vessels made in steel and equipped with safety devices such as pressure relief valves and excess flow valves, and are regularly inspected and pressure tested. Details of chlorine containers are given in the publications of the Chlorine Institute.

Chlorine is also transported by pipelines. Such pipelines range from 1 to 6 in. in diameter. The longest run quoted is 10 000 ft of a 4 in line.

The authors' tabulation of chlorine accidents has already been given in Table 18.30. Storage of chlorine had not resulted in a single accident in the USA in the 40 years up to 1974. There have been several accidents in small storages in Europe, but it is possible that these have been due to the presence of water and the resultant corrosion; this is avoided in good modern practice.

Barge accidents are few, possibly because the barge structure forms a means of protection for the chlorine tanks, in contrast to the situation on petroleum barges, where the barge shell is also the containing wall.

Rail tank car accidents have been more frequent. One major cause of these, the cracking of the tank at the anchor, which is the attachment of the tank body to the frame, has been largely eliminated by replacing forged anchors with welded ones, but accidents still occur, mainly by derailments and collisions. Department of Transportation (DOT) statistics indicate that there are approximately five rail tank car accidents per year which result in the release of chlorine, but only a small proportion of these involves a multiton release.

Road tanker transport is less significant and gives rise to fewer accidents.

Accidents with containers of 1 ton or less are important. As Figure 18.10 shows, some of the worst accidents have resulted from releases from cylinders and other small containers. This is probably because the releases took place in buildings and other confined spaces. It is considered by the authors that the dominant hazard is transport of chlorine by rail tank car. Some chlorine transport accidents are described in Case Histories A94, B66 and B67.

It was estimated by the Chlorine Institute that the proportions of chlorine distributed by the different modes of transport in the years 1965 and 1966 were: rail, 70%; pipeline, 20%; and barge, 7%. Thus, assuming the same division, some 3.1×10^6 ton of chlorine were transported by rail in 1972 and this figure was expected to grow to about 7.2×10^6 ton by 1990. It is clear from these data that rail transport is the dominant mode of distribution.

The problem principally considered by Simmons, Erdmann and Naft, therefore, is incidents involving rail tank cars carrying 90 ton of chlorine. Their treatment consists of the determination of (1) the frequency of accidents involving chlorine spillage and (2) the number of fatalities resulting from spillage.

Statistics kept by the Railroad Administration of the DOT and by the Chlorine Institute showed that there are some 7000 chlorine rail tank cars in service, that each tank car makes an average six trips a year and that the average length of journey is 250 miles. Since 1930 there have been seven accidents in which most or all of the contents of a tank car have been lost, although three of these were due to the failure of a forged tank anchor, a cause presumably now eliminated. On the other hand, the amount of traffic is increasing. On balance, therefore, the best estimate of accident frequency from these data is once in 10 years.

Other data are available on accidents to the same type of rail tank car as is used for chlorine in the transport of liquid ammonia and LPG. In a study covering 1966–70 the Association of American Railroads (AAR) found that for this type of rail tank car and for all cargoes, including chlorine, the accident rate was 2.3×10^{-5} per trip. Applied to the approximately 40 000 trips (7000 tank cars $\times$ 6 trips/y) made by chlorine tank cars these data would give an accident rate of once per year. The order of magnitude difference between this and the previous figure remains an unresolved discrepancy, but the authors suggest that it may be due to the way in which chlorine shipments are handled. They tentatively adopt the lower figure of 0.1 accidents per year.

Table 18.36 *Accident scale–frequency relationship for chlorine rail transport accidents (after Simmons, Erdmann and Naft, 1974)*

Accident size (Potential deaths)	*Frequency* (events/y)
50–100	1.4×10^{-2}
100–250	1.0×10^{-2}
250–500	4.0×10^{-3}
500–1000	1.5×10^{-3}
1000–2500	1.2×10^{-3}
2500–5000	7.2×10^{-4}
5000–20 000	2.6×10^{-4}

The determination of the area of lethal dosage for spillage from a 90 ton tank car with flash vaporization of 17.5% of the tank contents, or 15.7 ton, was described above. This calculation is then combined by Simmons, Erdmann and Naft with the above estimate of frequency and with data on the frequency of meteorological conditions to obtain estimates of potential casualties.

The population density assumption made is that a large spill is equally likely anywhere along the rail shipping route. This assumption is not conservative, since data for all rail accidents indicate a somewhat higher frequency in urban areas, the higher speeds in rural areas presumably being more than balanced by the higher density of traffic and switching activities in towns.

Estimates of potential fatalities were made for some 13 different weather conditions and 9 population densities, making 117 permutations in all. Accidents were then divided into 7 size ranges and a histogram was constructed. There were some 75 accidents involving 50 or more potential fatalities and the average number of fatalities was 13 per year. The histogram data are approximately as shown in Table 18.36.

From these histogram data the authors derive for the number N of fatalities the density function $f(N)$

$$f(N) = 0.15N^{-1.61} \qquad [18.29.6]$$

Simmons, Erdmann and Naft quote unpublished work by G.D. Bell (n.d.) on toxic releases which likewise gives an exponent of -1.6 for Equation 18.29.4, although in this latter case there were insufficient data to determine a realistic value of the constant factor.

The fatalities calculated in this work are described as 'potential', because no allowance is made for the effectiveness of any post-accident action to limit the effects. In fact, public warning and evacuation would probably greatly reduce the number of deaths.

It should be noted in particular that the conditions which give the highest number of fatalities are those in which the wind speed is low and the time available for evasive action is relatively long. In such cases, therefore, it is more probable that evacuation will be effective and that the ratio of actual to potential deaths will be relatively low.

For the 40–year period covered by the data given in Table 18.30, 204 people were gassed and one killed (excluding the small release in the Philadelphia incident) in railroad chlorine accidents. This compares with a

value from the histogram data and equation 18.29.4). of 570 persons expected to be killed. The comparison indicates, on the one hand, support for Equation 18.29.6, in that the figures for people affected agree quite well, and on the other the effectiveness of evacuation, in that people fled and were gassed, but were not killed.

It is emphasized by the authors, however, that estimates of this kind involve many unknown factors, particularly in respect of accident frequency, and that the associated uncertainty is estimated to be a factor of 10.

The method described uses a mixture of historical data for accident frequency and estimation of the scale and frequency of the results of the accident.

As the authors point out, in some cases the historical data may be too sparse or non-existent, and then the accident frequency must also be estimated.

Simmons, Erdmann and Naft compare the risk to the whole US population from chlorine railroad accidents of 13 potential fatalities per year with other risks to which the public are exposed. These include estimated risks in the range of 10–100 fatalities per year from the failure of dams and in the same range for aircraft crashes (persons on the ground only).

Westbrook (1974) has made a comparative study of the relative hazards of the transport of chlorine by rail, road and pipeline by the principal UK producer, ICI.

Much of the work was concerned with the determination of accident data. Here difficulties were experienced because data tend to be reported in forms which are not readily convertible, e.g. ton-miles, vehicle-miles, train-miles. The approach adopted, therefore was to consider the transport of the entire amount shipped (200 000 ton/year) by each mode in turn.

The investigations involved the determination of (1) the frequency of significant accidents, (2) the probability that a significant accident results in a spillage, and (3) the number of fatalities resulting from a spillage.

The frequency of accidents was determined from accident records. The accidents referred to are 'significant' accidents. For rail, such an accident is the one which is judged to be potentially most dangerous, and includes all derailments and most collisions. Such accidents represent 32% of all reported train accidents. For road, a significant accident is one which results in injury or death and is what the police call a 'reportable' accident.

The relevant accident data for rail for 1971 were:

Capacity of rail tank car = 28 ton
Number of rail tank cars in chlorine train = 4
Number of rail journeys = $200\,000/(4 \times 28) = 1786$
Distance travelled per train journey = 160 mile
Total distance travelled as train journeys = 1786×160
= 286 000 train-mile/year
Accident frequency for goods trains = 3.79×10^{-6} accidents/train-mile
Accident frequency for chlorine trains
= $286\,000 \times 3.79 \times 10^{-6}$
= 1.08 accidents/year

The data for road were:

Capacity of road tanker = 19 ton
Number of vehicle journeys = $200\,000/19 = 10\,526$
Distance travelled per journey = 160 mile
Total distance travelled = $10\,526 \times 160$
= 1.684×10^6 vehicle-mile/year
Accident frequency for goods vehicles = 2.03×10^{-6} accidents/vehicle-mile
Accident frequency for chlorine vehicles
= $1.684 \times 10^6 \times 2.03 \times 10^{-6}$
= 3.42 accidents/year

The above data refer to all journeys, but on average half the journeys made are with empty tanks. Thus the numbers of significant accidents by the two modes of transport become:

Accident frequency for rail transport (loaded)
= 0.54 accidents/year
Accident frequency for road transport (loaded)
= 1.71 accidents/year

The probability that a significant accident results in a spillage was estimated from consideration of mechanical strength of the tank and of the force of impact. It was thought initially that at normal road tanker speeds of about 30 mile/h there might not be sufficient energy to puncture the pressure vessel. It was shown, however, by tests and calculations, that puncture can occur under expected accident conditions and that all road tanker accidents should be assumed to be potential spillage accidents.

The probability of puncture is a function of kinetic energy. It was found, however, that the average speeds of chlorine rail tank cars and road tankers are almost equal. Thus it was possible to consider damage levels in terms of mass only.

A rail tank car in a train is subject to wagon-to-wagon collisions. A relation was derived for the damage to a wagon in a train involved in a front-end collision with an immovable object. It is assumed that the damage is proportional to the mass of the wagon involved and that it is shared equally between the wagons. Then for the first wagon behind the engine the damage D is proportional to its own mass W for the first collision, which is with the engine, to $\frac{1}{2}W$ for the second collision, which is between the first and second wagons, to $\frac{1}{3}W$ for the third collision, which is between the first three wagons, and so on. Thus:

$$D_1 = W(1 + \tfrac{1}{2} + \tfrac{1}{3} + \tfrac{1}{4} + \ldots) \qquad [18.29.7a]$$

where D_i is the damage to wagon i (mass units) and W is the mass of a single wagon (mass units). For the second wagon

$$D_2 = W(\tfrac{1}{2} + \tfrac{1}{3} + \tfrac{1}{4} + \ldots) \qquad [18.29.7b]$$

And for the nth wagon in a train of N wagons

$$D_n = \left(\frac{1}{n} + \frac{1}{n+1} + \frac{1}{n+2} + \frac{1}{n+3} = \ldots + \frac{1}{N}\right) \qquad [18.29.7c]$$

A group of m adjacent chlorine rail tank cars can occupy $N - m + 1$ positions in the train. Then, assuming $W = 1$, the average damage per train D_{tn} is

$$D_{\text{tn}} = \frac{1}{N - m + 1} \sum_{n=1}^{N-m+1} (D_n + D_{n+1} + D_{n+2} + D_{n+3}) \qquad [18.29.8]$$

and the average damage per rail tank car D_{rc} is

$$D_{rc} = \frac{D_{tn}}{m} \quad [18.29.9]$$

The probability that the rail tank car will be punctured is proportional to the average damage.

If the train has 25 wagons ($N = 25$) and if there are four chlorine rail tank cars ($m = 4$)

$D_1 = 3.82$ mass units
$D_2 = 2.82$ mass units
$D_3 = 2.32$ mass units
...
$D_{25} = 0.04$ mass units

and

$D_{tn} = 3.645$ mass units
$D_{rc} = 0.911$ mass units

A chlorine road tanker and a rail tank car have a mass of 30 and 40 ton, respectively. Thus on the assumption that the probability of puncture is proportional to the mass, the ratio r of the probability of puncture for a rail tank car to that for a road tanker is as follows:

First position behind engine $r = \frac{3.82}{30} \times 40 = 5.1$

Average position in train $r = \frac{0.911}{30} \times 40$

$= 1.22$ for one tank car
$= 4 \times 1.22$
$= 4.86$ for train

The analysis is relevant to the positioning of chlorine rail tank cars in the train in that it indicates that for a front-end collision the least desirable position is immediately behind the engine.

Collisions other than front-end collisions are also considered by Westbrook. A head-on collision of two trains is considered no worse since, although more energy is involved, it is distributed among more wagons. On the same argument, a back-end collision of two trains is less serious, since the energy involved is no greater than a front-end collision, but it is distributed among more wagons.

An absolute estimate of the probability of a spillage given a significant accident was made from the North American data for rail furnished by the Chlorine Institute and shown in Table 18.37. Over the period 1960–72 there were 67 accidents to chlorine trains, of which six resulted in spillage of chlorine. The probability of chlorine spillage in a significant rail accident in North America was therefore taken as $6/67 = 0.09$.

This use of North American data was necessary, because equivalent data for the UK were lacking. American conditions differ, however, in a number of respects:

	UK	*North America*
Rail tank car mass	40 ton	87 ton
Average No. of goods wagons	25	100
Average No. of chlorine rail tank cars	4	2
Average speed	15 mile/h	23 mile/h

The American pressure vessel is 0.753 in thick compared with the British 0.526 and requires 26% more energy to pierce it.

Since under American conditions there are two rail tank cars in a 100–wagon train

$D_{tn} = 1.967$ mass units

But the mass units in this case are greater than those for the British case by the following factor, which takes into account the different kinetic energy:

Table 18.37 *Accidents in bulk carriage of chlorine in the USA and Canada (Westbrook, 1974) (Courtesy of Elsevier Publishing Company)*

	Significant leakage – no accident	*Accident*	*Accident, leakage*	*Accident, fire*	*Accident, leakage, fire*	*Accident, leakage, death*
1961		3				1
1962	1	1				
1963		1			1	
1964		4	1			
1965		8				
1966		1	1	1		
1967		7		1	1	
1968		7				
1969		6				
1970		8		1		
1971	1	8		1		
1972		4	1			
Total	2	58	3	4	2	1

$$\frac{87}{40} \times \left(\frac{23}{15}\right)^2 \times \frac{1}{1.26} = 4.05$$

Then the probability of chlorine spillage in a significant rail accident in the UK is estimated as

Probability of chlorine spillage for rail transport

$$= 0.09 \times \frac{3.645}{1.967} \times \frac{1}{4.05} = 0.041 \text{ occasions/accident}$$

Frequency of chlorine spillage for rail transport

$$= 0.041 \times 0.54 = 0.022 \text{ spillages/year}$$

and the probability of chlorine spillage in a significant road accident in the UK is

Probability of chlorine spillage for road transport
$= 0.041/4.86 = 0.0084$ occasions/accident
Frequency of chlorine spillage for road transport
$= 0.0084 \times 1.71 = 0.0144$ spillages/year

The number of fatalities resulting from a spillage depends on the following factors listed by Westbrook: (1) warning time; (2) emission from the tank; (3) dispersion over the downwind area; (4) population density in the area affected; (5) chance of escape.

The time elapsing before warning is given was estimated as 24 minutes for rail and for road. A random sample of 17 accident reports from the files of British Rail headquarters at Marylebone indicated that it took, on average, 12 minutes for the first public aid vehicle (police, fire or ambulance) to arrive at the scene of a rail crash. It was considered that this delay was no longer than might be expected for a road accident. The figure of 12 minutes was then doubled to allow for the communication of an effective warning to the public.

For emission it was assumed that the initial temperature in the tank was 38°C, that the puncture holes in the vapour space were 19 in. and those in the liquid space were 7 in., and that the latter hole was at a level which allowed only $\frac{1}{3}$ of the tank contents to remain in the tank. Under these conditions it was estimated that some $\frac{2}{3}$ of the chlorine liquid would flash off or form spray and vaporize within the first 4 minutes and that the remaining liquid would boil off over a period of about 2 hours.

The situation for dispersion is intermediate between an instantaneous and a continuous release. At a given point downwind there is a distance/velocity lag before the cloud arrives, then the concentration rises rapidly to a maximum as the instantaneous release cloud passes and then falls to a steady value as the continuous release plume becomes established. Dispersion calculations were done using the Pasquill method assuming a 5 mile/h wind speed and a dangerous chlorine concentration of 20 ppm. On the assumption that 24 minutes would elapse before effective warning would be given, the chlorine cloud would have drifted 2 miles. Then the areas in which a dangerous chlorine concentration would exist were estimated to be:

Area of dangerous chlorine concentration for rail spillage
$= 0.076$ mile^2
Area of dangerous chlorine concentration for road spillage
$= 0.052$ mile^2

Estimates of population density were made on the rail and road routes to one of the principal customers for chlorine. Estimates of the number of people within, on average 100 ft, of an accident were made by travelling the road route by car and the rail route by brake van. The numbers obtained were 3 and 5 persons on the rail and road routes, respectively. But, since road accidents tend to give rise to congestion, the figure for the road case was increased to 20. Other coarser scale surveys of the routes were made using maps, but in this case there was little difference in population density, and the average value of 700 persons/mile^2 applicable to Great Britain was taken. Then, applying this population density to the areas at risk from spillage and including those people within 100 ft:

Number of people at risk from rail spillage
$= 0.076 \times 700 + 3 = 56$
Number of people at risk from road spillage
$= 0.052 \times 700 + 20 = 56$

The chances of escape were estimated as follows. The Chlorine Institute data given in Table 18.37 indicate that there were eight substantial chlorine spillages in North America in the period 1960–72. If on each occasion $\frac{2}{3}$ of the tank contents had been released, then calculations show that the area affected within a 24–minute period would have been 0.133 mile^2. With an average population density of 60 persons/mile^2 the number of people at risk from the eight incidents would have been

$$8 \times 0.133 \times 60 = 64$$

But in fact in these incidents 156 people received medical treatment and one person died. These figures suggest that the population density at the scene of the accidents may have been higher than average and that the assumed warning period of 24 minutes may be too low. Press reports of the incidents suggest that a high proportion of those at risk received medical attention.

Applying a ratio of 1 death in 156 to the number of people at risk from either a rail or a road spillage gives:

Frequency of fatalities from rail or road spillage

$$= 1 \times \frac{56}{156} = 0.359 \text{ deaths/spillage}$$

Then:

Frequency of fatality from rail transport
$= 0.022 \times 0.359$
$= 0.0079$ deaths/year
Frequency of fatality from road transport
$= 0.0144 \times 0.359$
$= 0.0052$ deaths/year

Westbrook also discusses the sensitivity of the calculations to changes in the assumptions. He considers three such changes:

A Rail and road tankers both suffer one significant accident per year more than the national average.
B Damage estimate in rail crashes is pessimistic and is reduced by factor of 2.
C Estimate of number of people at risk in road accidents is optimistic and is increased by 50.

The frequency of fatalities then becomes

Case	*Frequency of fatalities*	
	(rail deaths/year)	(road deaths/year)
A	0.023	0.0082
B	0.0039	0.0052
C	0.0079	0.0098

These calculations suggest that neither rail nor road has a marked advantage over the other from the point of view of safety in the transport of chlorine.

The study also considered the distribution of chlorine by pipeline and by vehicles with refrigerated atmospheric tanks. For the pipeline the case considered was a line of 4. in diameter and 20 mile long carrying 25 ton/h of chlorine at 15°C for 2000 h/year. From a study of pipeline records in the UK and the USA, it was concluded that a pipeline of this length might sustain damage once in 10 years and that on one occasion in 10 there would be a massive release of chlorine. The fracture was assumed to occur between excess flow valves 2 miles apart, $1\frac{1}{2}$ miles from one valve and $\frac{1}{2}$ mile from the other, allowing emission of chlorine from both ends. It was further assumed that the excess flow valves would take 30 seconds to close. The calculations involved the difficult problem of emission under two-phase flow conditions. The results obtained were

Initial flow rate of chlorine = 60.3 ton/h per 4 in. orifice
= 120.6 ton/h total
Total quantity of chlorine emitted in 24 min = 28.4 ton
Size of cloud of dangerous concentration = 0.101 mile^2
Number of people at risk = 74
Frequency of fatalities from pipeline break
= 0.48 deaths/break

$$= \frac{0.48}{10 \times 10}$$

= 0.0048 deaths/year

The pipeline conveys 50 000 ton/y of chlorine over 20 miles. Comparison with rail or road transport requires that they be put on the same basis. If this is done, the frequency of fatalities is 0.0005 and 0.00032 deaths/year for rail and road transport, respectively. Therefore rail and road transport appear to be an order of magnitude safer than a pipeline.

It may be noted, however, that the assumption made by Westbrook on the frequency of damage to a chlorine pipeline is perhaps pessimistic. Information on pipeline failure rates is given in Chapter 23.

The transport of chlorine using refrigerated vehicles has not been studied so thoroughly at the time of writing. Preliminary work suggests that low temperature transport would be safer, perhaps by a factor of about 4, but it would not affect the choice between rail and road.

This work of Westbrook illustrates an approach to the assessment of the hazards of transport of toxic substances. Many assumptions and uncertainties are involved and the results are both approximate and tentative. It should be emphasized that the study is concerned with a comparative assessment of the different modes of transport, particularly rail and road. Such comparative assessment is difficult and demands accurate estimates if the results are to be meaningful in discriminating between transport modes.

18.30 Other Chemicals Hazard Assessment

Solomon, Rubin and Okrent (1976), from a study on the hazards of the storage of chemicals, give estimates of the areas affected by and the lethality of releases of chlorine, acrylonitrile, hydrogen cyanide and parathion. Parathion has the formula $(C_2H_5O)_2PSOC_6H_4NO_2$ and is much heavier than air.

They consider both instantaneous and continuous releases and use the Pasquill–Gifford equations. The equations used are, for instantaneous and continuous releases, Equations 15.16.40 and 15.16.41, respectively, and for dosage, Equation 15.16.66a. The values of the dispersion coefficents used are those given by Equations 18.29.3 and 18.29.4.

The relations assumed between dosage and fatalities or injuries for the chemicals studied are given in Table 18.38. The lethal dosages used are as follows:

Chlorine	40–60 ppm for 30–60 min
Acrylonitrile	200–400 ppm for 30 min
Hydrogen cyanide	100 ppm for 1 min
Parathion	20 mg (oral)
(lethal dose)	30 mg (dermal)

The authors refer to these as LD_{50} lethal doses, but in terms of the terminology used here the first three are strictly LCt_{50} lethal dosages.

The base scenario considered for all the chemicals is a release rate of 100 kg/s with 20% flash-off for 30 minutes exposure in an area of a population density of 1000 persons/km^2 under stability conditions Pasquill category A and at a wind speed of less than 2.5 m/s. For parathion it is assumed that there is no deposition from the air to the ground.

Cases without and with evacuation are considered. With evacuation the evacuation half-time was 30 min. Some results obtained are shown in Table 18.39. Of the 12 000 deaths calculated for chlorine, about 3000 occur as a result of the initial flash-off and the remainder as the result of the subsequent steady flow.

Assuming a tank rupture rate of 1×10^{-6}/tank-year and the probability of the assumed meteorological conditions as 5×10^{-2}, the frequency of the maximal chlorine accident considered is estimated by the authors

Table 18.38 *Assumed relationship between dosage and fatality for toxic releases (after Solomon, Rubin and Okrent, 1976)*

Lethal dosage (%)	*Assumed mortality* (%)	*Assumed decrease in life expectancy* (years)
<1	0	0
1–10	5	0.08
10–25	10	0.5
25–50	20	1
50–100	40	5
100–200	65	10
>200	95	20

Table 18.39 *Effects of releases of some toxic chemicals without and with evacuation (after Solomon, Rubin and Okrent, 1976)*

Chemical released	*Evacuation*	*Fatalities*
Chlorine	No	12 000
	Yes	9800
Acrylonitrile	No	5500
	Yes	4600
Hydrogen cyanide	No	49 000
	Yes	39 000
Parathion	No	9600
	Yes	6600

as 5×10^{-8}/year for such a storage tank in such an area.

18.31 Hazard Assessment Methodology

Developments in the methodology for the hazard assessment of toxic releases have occurred in a number of areas, including the following: (1) source term, (2) heavy gas dispersion, (3) concentration fluctuations, (4) mitigation by barriers and sprays, (5) mitigation by shelter and evacuation, (6) toxicity relations, (7) degree of injury, (8) specific gases, (9) population exposure, (10) plant layout, (11) warehouse fires and (12) computer aids.

18.31.1 Source term

One area in which the hazard assessment of toxic releases has become much more realistic is in the handling of the source term. Much early work was based on the outright failure of a pressure vessel and, often, the ejection of its entire contents.

It is recognized that the total failure of a pressure vessel is very rare. Better estimates are available of lesser failures such of those of pipework. Allowance is made for emergency action such as the closure of emergency isolation valves.

As described in Chapter 15, methods have been developed to guide the choice between continuous and quasi-instantaneous release models, and thus reduce the proportion of cases where the more pessimistic quasi-instantaneous case is assumed.

Progress has been made in the modelling of the release of pressurized or refrigerated fluids. Models are available for the behaviour of the inventory on rupture of a pressure vessel and for two-phase flow from leaks on pipework. The models for evaporation from the pool formed following emission of a liquid are also much improved.

18.31.2 Gas dispersion

In most cases, the vapours of the principal toxic liquids exhibit heavy gas behaviour and great strides have been made in heavy gas dispersion modelling. The methods now available, which include models for manual use such as the *Workbook* models, computer codes such as HEGADAS and the three-dimensional models as well as physical modelling using wind tunnels, provide a set of tools capable of handling not only dispersion over flat, unobstructed terrain, but also the effects of slopes, buildings, barriers and water sprays. The concentration estimates yielded by these heavy gas models tend to be quite different from those of passive gas dispersion models.

18.31.3 Concentration fluctuations

It has long been appreciated that there are considerable fluctuations in the concentrations at a fixed point in a gas cloud. Methods are now available which allow estimates to be made of these concentration fluctuations. It is also appreciated that these fluctuations must have some influence on the effective toxic load, as pointed out by R.F. Griffiths and Harper (1985). Methods of treating this aspect are given by D.J. Wilson and Sims (1985), D.J. Wilson (1991a) and J.K.W. Davies (1987, 1989a).

18.31.4 Mitigation: terrain, barriers and sprays

As just stated, the heavy gas dispersion models available can now treat situations where mitigatory features exist. Since the typical release occurs in a works, the gas dispersion will be strongly affected by the presence of buildings, which tend to enhance the dispersion. An illustration of a hazard assessment of a toxic release in the presence of buildings is given by Deaves (1987b).

Further mitigation can be obtained by the use of barriers and sprays, and models are available to allow these to be taken into account in the assessment (e.g. Meroney, 1991).

18.31.5 Mitigation: shelter and evacuation

Another major form of mitigation occurs where the exposed population remains indoors and thus benefits from shelter. Methods have been developed to estimate the indoor concentration–time profile, and hence toxic load, given the profile of the outdoor concentration. The development of models for the effect of shelter is illustrated by the work of P.C. Davies and Purdy (1986) and D.J. Wilson (1987, 1990, 1991b).

18.31.6 Toxicity relations

The form of injury relation generally used in the hazard assessment of toxic releases has been the probit equation. An account has been given above of the development of probit equations for this purpose.

The use of probit equations involves a number of problems. In large part these reflect the basic difficulty of determining the human response to a toxic load. One problem is that a probit equation is available only for a relatively small proportion of toxic gases. Even where a probit equation exists, it may be subject to considerable uncertainty. The accuracy of the relation can be expected to be highest close to the LC_{50}, but relatively low when extended to an LC_{05} or LC_{01} level. Yet in many cases the number of persons exposed to these lower loads is much higher than that for those exposed to the higher load; where there is a *cordon sanitaire* around the site, as there usually is to some degree, the difference is increased.

There has been some exploration of alternatives to probit equations. The use of the IDLH value as an alternative to the probit equation in hazard assessment has been explored by MacFarlane and Ewing (1990).

Particularly where the purpose of the hazard assessment is to identify the contour for a particular level of

toxic effect, as in land use planning, use may be made not of a probit equation but of some fixed toxic load, such as the HSE SLOT value.

18.31.7 Degree of injury

Whereas the effect commonly estimated in hazard assessments of toxic releases has tended in the past to be the number of fatalities, there is some trend to estimate lesser degrees of injury. Thus the HSE SLOT value is a toxic load which is estimated not to be fatal to the vast majority of persons exposed. However, this type of criterion tends to be used not to determine the total number of persons exposed to the toxic load but the location of the contour around the site where the load will occur.

18.31.8 Specific gases

There have also been significant advances in the characterization of the toxicity of a number of common industrial gases, as described in Sections 18.15–18.21. In particular, reference may be made to the CPD *Green Book* probit equations, the HSE SLOT values and the toxicity estimates and probit equations of the MHAP.

18.31.9 Population exposure

Another area which has become more sophisticated is the characterization of the exposed population. As described in Chapter 9, there now exist what are, in effect, population exposure models, such as those given by Petts, Withers and Lees (1987) and in the *Green Book* (CPD, 1992b).

18.31.10 Plant layout

Increasingly, the effect of flammable and toxic releases is taken into account in plant layout, although the extent to which this is practical is greater for flammable and explosive materials than for toxic ones. An account of the work of Mecklenburgh (1985) on the use of hazard assessment in plant layout is given in Chapter 10.

18.31.11 Warehouse fires

Another type of toxic hazard is that arising from warehouse fires. Most work on the quantitative treatment of this hazard is relatively recent. It includes the work of D.A. Carter (1989), G.T. Atkinson, Jagger and Kirk (1992) and G.T. Atkinson and Jagger (1994).

18.31.12 Computer aids

The computation either of the consequences of a toxic release or of the risk to the population around an industrial site or along a transport route is a natural application for computer codes, and a considerable number of codes are available. Accounts of certain codes such as WHAZAN, SAFETI and RISKAT are given in Chapters 9 and 29.

18.32 Notation

C concentration
k_1, k_2 constants
LC_i concentration lethal at i% level
LCt_i concentration–time product lethal at i% level
LD_i dose lethal at i% level
LL_i toxic load lethal at i% level
T exposure time interval
Y probit

Section 18.3

c concentration
d dose
D dose rate
D_o dose
k_e elimination constant
L toxic load
m index
t time
$t_{\frac{1}{2}}$ half-life
V apparent volume of distribution of chemical in body
X mass of chemical in body

Section 18.6

C_i time-weighted average concentration of ith component
L overall occupational exposure limit
L_i occupational exposure limit of ith component

Section 18.11

c concentration
C concentration (ppm)
D dosage
k constant
L toxic load
L^* toxic load (alternative formulation)
m, n indices
t time
T time interval (min)

Section 18.13

C_{O2} concentration of oxygen in liquid phase (mol O_2/ml fluid)
D_L pulmonary diffusion capacity (ml/min (mm Hg))
D_{LCO} pulmonary diffusion capacity for carbon monoxide (ml/min (mm Hg))
D_{LCO2} pulmonary diffusion capacity for carbon dioxide (ml/min (mm Hg))
D_{LO2} pulmonary diffusion capacity for oxygen (ml/min (mm Hg))
ERV expiratory reserve volume (ml)
f respiration rate (breaths/min)
F_{AO2} concentration of oxygen in alveolar space (ml O_2/ml air)
F_{EN2} concentration of nitrogen in exhaled air (ml N_2/ml air)
F_{EO2} concentration of oxygen in exhaled air (ml O_2/ml air)
F_{IN2} concentration of nitrogen in inhaled air (ml N_2/ml air)
F_{IO2} concentration of oxygen in inhaled air (ml O_2/ml air)
FRV functional reserve volume (ml)
H_{O2} Henry's law constant for oxygen (ml O_2/ml fluid (mm Hg O_2))
IC inspiratory capacity (ml)
IRV inspiratory reserve volume (ml)
P_{AO2} partial pressure of oxygen in alveolar space (mm Hg)
$P_{AO2'}$ equilibrium partial pressure of oxygen in alveolar space and above pulmonary capillaries (mm Hg)

$P_{O2'}$ equilibrium partial pressure of oxygen (mm Hg)
$P_{O2a'}$ equilibrium partial pressure of oxygen above arterial blood (mm Hg)
$P_{O2v'}$ equilibrium partial pressure of oxygen above venous blood (mm Hg)
RV residual volume (ml)
TLC total lung capacity (ml)
TV tidal volume (ml)
V_A alveolar space (ml)
$\dot{V}_A$ alveolar minute volume, alveolar ventilation (ml/min)
V_D anatomical dead space (ml)
V_E volume exhaled (ml)
$\dot{V}_E$ exhaled minute volume (ml/min)
$\dot{V}_I$ inhaled minute volume (ml/min)
$\dot{V}_{O2}$ rate of absorption of oxygen, oxygen consumption minute volume (ml/min)
V_T tidal volume (ml)
$\dot{V}_T$ minute volume (ml/min)
V_C vital capacity (ml)

Section 18.15
C concentration (ppm)
n index
T time interval (min)
V causative factor

Section 18.16
C concentration (ppm)
L^* load (ppm min)
T time interval (min)

Section 18.16.10
t time (min)

Section 18.17
C concentration (ppm)
t time (min)

Section 18.18
P probability of death
P_a probability that death is acute
ψ_1 inhalation rate factor
ψ_2 medical treatment factor

Section 18.19
A surface area of lungs (m^2)
C concentration of gas in atmosphere (mg/m^3)
D inhaled dose (mg)
D' inhaled dose per unit body mass (mg/kg)
D'' inhaled dose per unit area of lung (mg/m^2)
f safety factor
f_d extrapolation factor
t exposure time (min)
V_a minute volume (l/min)
W body mass (kg)

Section 18.29
Equations 18.29.1 and 18.29.2
C ground level concentration on axis of plume (m^3/m^3)
d downwind distance (m)
F stack correction factor
h vertical spread of plume at distance d (m)
H effective height of stack (m)
Q gas release rate (m^3/s)
u wind speed (m/s)
θ lateral spread of plume (deg)

Equations 18.29.3–18.29.6
A area of lethal dosage (km^2)
$f(N)$ density function for fatalities
k, k' constants
n, n' indices
N number of fatalities
u wind speed (m/s)
x distance in downwind direction (m)
σ_y, σ_z dispersion coefficients in cross-wind, vertical directions (m)

Equations 18.29.7–18.29.9
D_n damage to wagon n (mass units)
D_{rc} average damage per rail tank car (mass units)
D_{tn} average damage per train (mass units)
m number of adjacent chlorine rail tank cars
n wagon counter
N number of wagons in train
r ratio of probability of puncture of rail tank car to probability of puncture of road tanker
W mass of wagon (mass units)

19 Plant Commissioning and Inspection

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19.1 Plant Commissioning

The commissioning, or initial start-up, is a period when the plant is particularly at risk. It is also a time when equipment may be maltreated or damaged so that its subsequent operation is affected. Moreover, delays in bringing the plant up to full output can have a marked effect on the economics of the plant. For all these reasons it is essential to organize the commissioning of the plant efficiently and to allocate sufficient resources to it.

An account of plant commissioning is given in *Process Plant Commissioning* (Horsley and Parkinson, 1990), *Process Plant Design and Operation* (D. Scott and Crawley, 1992) and by Troyan (1960), Finlayson and Gans (1967), Kinglsey, Kneale and Schwartz (1968–69), Gans and Benge (1974), Unwin, Robins and Page (1974), Fulks (1982), Gans, Kiorpes and Fitzgerald (1983), Fraylink (1984), Ruziska *et al.* (1985) and Smet (1986).

In the following sections an account is given of plant commissioning and of some of its problems and hazards. It should be said at the outset, however, that in many cases these have been very successfully overcome by good organization and engineering so that, for example, large ethylene plants have been brought up to full output within about 3 days (Chementator, 1977 Jun. 6, 67; Oct. 24, 73). Selected references on plant commissioning are given in Table 19.1.

Extensive use is made during plant commissioning of checklists. It is common for a writer on the topic to include one or two such checklists. A rather comprehensive set is given by Horsley and Parkinson, both in the text and the appendices, as indicated in Table 19.2.

Table 19.1 *Selected references on plant commissioning*

Eames, Sturgis and Weeks (1959); Troyan (1960, 1961b,c); Lieber and Herndon (1965, 1973); Loen (1966, 1973); Bacchetti (1967); J.E. Baker and Burt (1967); Bopp (1967); Finlayson and Gans (1967); Garcia (1967); Holroyd (1967); Murray and Wright (1967); de Regules (1967); J.R. Bradley and Nimmo (1968); Finneran, Sweeney and Hutchinson (1968); Kingsley, Kneale and Schwartz (1968–69); MacNeish (1968); Feldman (1969); Lofthouse (1969); Matley (1969); Tucker and Cline (1970, 1971); Whyte (1970); Andrew (1971); Bacchelli and Bianco (1971); Clifton, Vinci and Gans (1971); McCallister (1971); Murphey (1971); Parsons (1971b); Swain and Hopper (1971); R.G. Wright (1971); Buyers (1972); Goldman (1972); G.M. Miller (1972); Ryan (1972); BCISC (1973/12); Galluzzo (1973); Godard (1973); A.J.Morton (1973); Asquith (1974); J.D. Baker (1974); Barnes (1974); Gans and Benge (1974); IChemE (1974/32); Mackey (1974); T. Robbins (1974); P.C. Russell and Herbert (1974); Spearing (1974); Turnbull, Buyers and Smith (1974); Unwin, Robbins and Page (1974); Voss and Ludbrook (1974); Gans (1976a); Anon. (1977 LPB 18, p.2); L. Pearson (1977a,b); Whiston (1977); British Gas (1978 Comm. 1104); Puckorius (1978); Vincent and Gent (1978); API (1981 Publ. 700); Westerman (1981); Fulks (1982); Gans, Kiorpes and Fitzgerald (1983); Fraylink (1984); Kletz (1984k); Ruziska *et al.* (1985); Smet (1986); Horsley and Parkinson (1990); Kingsley (1990)

Table 19.2 *Some checklists for plant commissioning (after Horsley and Parkinson, 1990)*

A Appendices

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Reservation checklist: pipelines and pipework	3.1
Reservation checklist: chemicals and hydrocarbons in	3.2
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Pressure vessels	5.2.1
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Instrument loop	6.3.1
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B Text

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19.1.1 Contract

The responsibility for the construction and commissioning of the plant is normally shared between the user company and its contractors, but the division of responsibility may vary considerably. The different types of contract are discussed by Horsley and Parkinson. The project may be predominantly in-house, utilizing a small number of subcontractors, or it may be undertaken as a 'turn-key' by a contractor. The contract may be fully reimbursable or fixed cost.

It is essential that the conditions of contract use unambiguous terminology and give clear guidance on the responsiblities of the parties for the various stages of the commissioning and for the associated documentation. Model conditions of contract for different types of contract are available and those of the Institution of Chemical Engineers (IChemE) are widely used for process plants, as described in Chapter 11.

The procedure developed by one UK process plant contractor to define responsibilities is illustrated in Table 19.3 (from Horsley and Parkinson). These authors give further demarcation schedules governing phases A–G of the project.

Table 19.3 *Demarcation between contractor and client of work and responsibility in construction and commissioning (Horsley and Parkinson, 1990) (Courtesy of the Institution of Chemical Engineers)*

Construction and pre-commissioning:
PHASE A Prepare plant/equipment for pre-commissioning/mechanical testing
PHASE B Prepare services: clean and pressure test systems
PHASE C Check and prepare major mechanical equipment, instrumentation, and protection systems
PHASE D Final preparations for start-up
Commissioning:
PHASE E Charge with feedstock, etc. Start up plant and operate
PHASE F Performance test and plant acceptance
PHASE G Remainder of maintenance period

PHASE	A	B	C	D	E	F	G
1 Control of works by:		Contractor construction				Client	
2 Basic responsibilities and phases for various categories of staff at site							
Construction		Site manager and team of construction specialists			Defects correction under contractor's direction		Return for corrective work
Contractor Comm		Witnessing inspection & testing			Advising start-up & operation of plant	Witnessing performance test	
			Training client's operators				
Client		Witnessing inspection & testing			Plant maintenance and normal adjustments by client		
			Operators receiving training		Preparing for start-up: starting up and operating plant		
Equipment vendors		Testing and commissioning presence on site				On-call to site to end of maintenance period	
3 On completion of construction			CERTIFICATE OF MECHANICAL COMPLETION/TAKING OVER CERTIFICATE				
					CERTIFICATE OF ACCEPTANCE OF PLANT PERFORMANCE		
						FINAL CERTIFICATE	

In the account which follows, it is convenient to assume that, unless otherwise stated, the project is a turn-key one undertaken by a major contractor.

19.1.2 Commissioning phases

The overall process of plant commissioning passes through a number of phases. It starts with the completion of erection. This term covers the end of installation of the equipment and is used sometimes, but not here, to cover also pre-commissioning. There then follows the phase of pre-commissioning. During this period there occur mechanical completion and pre-commissioning; installation and checking of the control system; and process commissioning.

By the end of process commissioning the various sections of the plant have been operated with process fluids. There then follows the performance testing in which the plant is operated and, if it meets its specification, accepted.

The activities during these phases may be illustrated by considering those in phases A–E of the contract scheme just mentioned. In broad terms, these are:

A Safety precautions; preparation of utilities; gland packing; preparation for line flushing.
B Commissioning utilities; machine rotation; pressure and leak testing; vessel cleaning; line flushing; relief value testing and re-installation.
C Chemical cleaning; machine alignment; lubrication systems; machine short running tests; instrumentation checks.
D Final preparations for performance testing.
E Charging of feedstock.
F Performance testing.

In the scheme described, the three areas of responsibility are supervision, trades and labour, and inspection. Essentially, the responsibility for the first lies with the contractor, and in phase C the vendor also; responsibility for the second is with the contractor up to phase D, when the client has a roughly equal input; and responsibility for the third passes increasingly from the contractor to the client over phases A to E. It is the client who carries out the performance testing of phase F.

19.1.3 Organization

It is important to organize the commissioning thoroughly and to provide the appropriate personnel. There is no simple model for the organization and personnel for commissioning. These depend on the nature of the process, the size of the plant, the involvement of other parties, such as licensors and contractors, and so on. What is essential is that the management allocate sufficient resources to do the job efficiently. The commissioning of a large plant is a major enterprise and failure to recognize this is likely to increase costs and hazards.

The main conditions for success in commissioning, as listed by Kinglsey (1990), are: an ably led, well balanced, well trained and committed commissioning team; a well structured relationship at senior level with site construction management and future operational management; thorough planning and implementation of preparations; adequate involvement in design stages and safety studies; meticulous attention to hazards and safety; ready availability of assistance from supporting disciplines; and an expeditious approval system for plant modifications.

Some aspects of the organization of plant commissioning are

(1) regulatory and code requirements;
(2) contractual arrangements;
(3) quality assurance;
(4) safety;
(5) personnel and other resources;
(6) budgetary control;
(7) planning and scheduling;
(8) modification arangements;
(9) communications;
(10) documentation.

The design, construction and operation of the plant are subject both to regulatory requirements and to the requirements of the codes and standards adopted. The latter should be clearly specified and there should be full information available about both sets of requirements.

The regulatory constraints on the discharge of gaseous effluents to the atmosphere and of liquid effluents to drains are generally of particular importance in commissioning.

The design, construction and operation of process plant are governed by quality assurance (QA). The extent of the QA system and its requirements varies between companies, but the trend is towards a formal system. The QA requirements need to be clearly laid down and arrangements put in place to ensure compliance. The QA system will generally cover the quality of the equipment and services supplied by the contractors and subcontractors and the installation and testing of the equipment. Where a full QA system is in operation, it will generally cover many of the aspects of plant commissioning discussed below.

Similarly, the plant design, construction and operation have to conform to the safety system and requirements. These too need to be clearly laid down and arrangements made to ensure compliance.

The definition of the relative responsibilities of contractors and the user needs to be particularly clear in the areas both of QA and safety.

Plant commissioning requires the deployment of a considerable resources of various kinds and its organization is in large part concerned with ensuring that they are available in sufficient quantity and at the right time. Foremost among these resources is a wide range of personnel, who are considered below.

The various activities which have to be performed as part of the commissioning should be reviewed and arrangements made to furnish the necessary resources, of personnel, equipment or services. Mechanical precommissioning, process commissioning and performance testing are phases which may well require special resources.

A budget needs to be prepared for the cost of these resources. Full allowance should be made both for extra costs incurred by the main categories of personnel involved, such as overtime, travel and accommodation, and for costs of back-up services. It may be necessary to separate the costs of pre-commissioning from those of commissioning. In some cases the two sets of costs are on a different basis, with the former being fixed price and the latter reimbursable.

Plant commissioning involves the planning and scheduling of a large number of activities. This aspect is treated in Section 19.1.5.

Arrangements need to be made to handle the plant modifications which are almost invariably required during commissioning. These should ensure that proposals to modify the plant are subject to review and that, where appropriate, the proposal is referred back to the design authority. Steps should be taken to ensure that this process is rapid and does not cause undue delay in the commissioning. This aspect is treated in Section 19.1.10.

Communications between the parties involved are always important in process plants and never more so than during plant commissioning. The information needs and the communication arrangements should be reviewed. Relevant aspects include documentation, written communications and meetings.

It should be arranged that the necessary documentation is available throughout the various stages of the project and that at termination of the commissioning the project is adequately documented.

It has been not uncommon that the commissioning period involves a series of crises, but this is not the most efficient way of doing it. As it has been put by Horsley (1974):

> It is also evident that the fun and personal satisfaction of being in the thick of things, having a tremendous degree of responsibility, working long hours and so on, are not efficient ways to start up a plant. In fact, an efficient start-up without the emergence of numerous challenging technical problems would probably be slightly dull and disappointing to technologists and experts.

19.1.4 Personnel

Responsibility for the commissioning should rest with a single individual. It is normal to appoint a commissioning manager who has this responsibility. For the case considered, that of a turn-key project, the commissioning manager is appointed by the contractor.

The typical composition of a contractor's commissioning team for a large ammonia plant is given by Horsley and Parkinson as a commissioning manager and deputy, four shift leaders, four assistants, a chemist, and mechanical, electrical and instrument specialists.

Where the project is done in-house, a common practice is to appoint a plant manager for the new plant some time in advance to let him familiarize himself with it, and to make him the commissioning manager. The job of the project manager is normally a separate one. Experience indicates that it is usually not good practice to attempt to combine the roles of project manager and commissioning manager. The commissioning team for an in-house project should be a strong one, with good technical capability and relevant experience. The team may consist of the personnel assigned to the plant supplemented by others who are brought in for the limited period of the commissioning only. It is necessary that the commissioning manager should be able to command the resources necessary to carry through the commissioning. Unforeseen problems can often result in considerable demands on resources. It may be desirable, particularly on large projects, to create an additional troubleshooting team. The organization of an extra field work team for this purpose has been described by Horsley (1974). Some of the many variations in commissioning team composition are described by Troyan (1960), Finlayson and Gans (1967) and Garcia (1967).

There are many variations in the ways of organizing the management team for commissioning. One is to design and impose the organization. An alternative, described by Horsley (1974), is to let this evolve by negotiation of roles among the managers with division of 'ownership' of particular features among them.

During commissioning there is likely to be conflict between individuals. This may be due, to some extent, to clashes of personality, but it is generally due mainly to differences of role and hence viewpoint which are inherent in the situation.

There is also a need for specialists, particularly with regard to proprietary items such as rotating machinery. Many problems which would otherwise prove difficult and time-consuming can be resolved if an expert is present at the right time.

The workload of individuals should be checked to ensure that it is not extreme. If someone is excessively overloaded and tired, he tends to become both less effective and more prone to error.

19.1.5 Planning and scheduling

Plant commissioning requires the co-ordination of a large number of activities carried out by many different people. Some aspects for which planning is particularly important include:

(1) commissioning activities –
  (a) pre-start-up activities,
  (b) initial start-up;
(2) budgets;
(3) documentation;
(4) recruitment;
(5) training.

The design and construction of a large process plant is normally scheduled using such methods as the project evaluation and review technique (PERT) and critical path scheduling (CPS). Usually these methods are implemented on a computer.

The scheduling of commissioning may be done as a separate exercise. An account of such scheduling has been given by Gans and Benge (1974), who quote typical figures of effort required of 1000 man-hours for a major project, or alternatively, 3 man-hours per major piece of equipment.

The method of scheduling is broadly as follows. All activities are broken down into their constituent parts. The man-hours and machine-hours needed to perform each activity are determined. The length of time required to perform the activity is calculated on the basis of the availability of men and machines. The duration of the activity is then assessed, taking account of such factors as running-in time. The conditions at which work can begin on the activity are then determined.

Again methods such as PERT and CPS may be used, but it is more common with commissioning than it is with design to do the scheduling by hand, using aids such as bar charts and arrow diagrams.

Modifications are then made such as speeding up an activity or paralleling activities. When this has been done, it is possible to calculate the slack, which is the difference between the earliest and latest time at which an activity can start, to work out programmes for a day or a week, to determine the resources of men and machines required and to assess the expenditures involved.

In many large plants critical path features are the reactors or the instrumentation.

It is easy to incur extra expenditure during commissioning and it is necessary to exercise close control on costs by controlling budgets for the various cost centres.

The communication of information is crucial in commissioning and it is essential to ensure that adequate documentation is available at the time when it is needed. Planning should include, therefore, a review of the documentation required.

The recruitment of personnel needs to be carefully planned. There is usually some uncertainty about the precise start time of various activities and this makes recruitment something of a problem. The problem is aggravated if there are difficulties at the recruitment end. In view of the uncertainties, recruitment in advance of requirement may be necessary, but it should be borne in mind that an excessive period waiting to start work can be demoralizing.

The training of both the management and the workforce needs to be planned. Important aspects are the scheduling and documentation of training.

19.1.6 Management preparation and training

The effectiveness of the commissioning depends to a considerable extent on the thoroughness of preparation by management. The commissioning manager normally prepares himself by studying the process and the plant, by visiting or working on similar plants, by involvement

in the project through work on design committees, by preparing plant documentation and operator training schemes, and so on.

There are some particular aspects on which he is well advised to brief himself thoroughly. One is process information and knowhow which has been purchased from outside. If problems arise in a bought-in process, it tends to be more difficult to put them right. Somewhat similar considerations apply to proprietary equipment, such as package units and complex machinery. It is also desirable for him to have a good grasp of the general economics and contractual features of the project. These range from raw material supply contracts to acceptance conditions for equipment.

It should not be assumed that it is only the process operators who need preparation and training for commissioning. These are required by management also. Some of the training requirements of the plant manager, and in particular the safety aspects, are discussed in Chapter 6.

19.1.7 Operations preparation and training

The operation of process plant requires the creation of a large number of systems and procedures. Many of these have to be formulated by the plant manager prior to and during commissioning.

The operating instructions are particularly important. These should be drafted early on, so that they can be used for operator training, but they are likely to need some modification in the light of operating experience.

It is also necessary to create a system of process records. The process log kept by the operator is one element in this, but there are numerous other records required for management purposes.

A process plant often receives its raw materials from or sends its products and/or by-products to other plants. The commissioning of such a plant tends to involve some degree of disruption of these plants. There is need, therefore, to co-ordinate the initial start-up so as to minimize such disruption. It may also be necessary to make arrangements to deal with unusable materials produced during the start-up, such as off-specification product.

Another feature which requires consideration is laboratory analysis and quality control. Safe operation requires a capability to analyse the material in the plant and ensure that it is within acceptable limits. This means working out methods of sampling and analysis, devising suitable tests and setting acceptance levels for raw materials, intermediates and products. It is also necessary to specify the associated paperwork.

The main training of the process operators is usually carried out jointly, during commissioning, by the training department and the plant management. The principal objectives of the training are to familiarize the operators with the chemicals handled, with the nature of the equipment and its location on the plant and with the procedures for operating the plant. A more detailed account of some of the principles and content of the training is given in Chapters 14 and 28 and a list of some of the documentation required for training is given in Chapter 6. Specific training in safety and loss prevention should be worked in with the other training material.

It may be appropriate to use lectures for the communication of certain basic information, but in general participative methods are likely to be more effective, and the commissioning situation lends itself well to the use of such methods. Workshops may be used to familiarize personnel with the hazards and with precautions and procedures. In some cases use is made of a simulator to provide training in normal operating and emergency procedures.

Further training is obtained on the plant itself, where the trainees become familiar with the layout and learn to operate equipment and instrumentation. Testing with safe fluids provides particularly valuable experience. Often a strong team spirit develops during this period of training.

The operators should become familiar at an early stage with the hazards of the materials, the plant and the process and the alarm, fire and emergency systems. There should be drills for evacuation and fire fighting.

The commissioning environment is one where participation by the whole workforce is natural. It offers the opportunity, if management is so minded, to build the participative culture required for total quality management.

Generally, the training activities reveal certain inadequacies in the procedures and these should be rectified. The appropriate changes should be made in the documentation.

Usually much of the instruction is done by managers and supvervisors who can benefit greatly from this, since instructing others is an effective way of learning. It is necessary to allow a sufficient number of management personnel to ensure that training is effective. It is a not uncommon experience that the level of training achieved at the end of the commissioning period is not bettered during the subsequent life of the plant.

Further accounts of process operator training during commissioning are given by Finlayson and Gans (1967), de Regules (1967), Kingsley, Kneale and Schwartz (1968–69) and R.Parsons (1971a).

19.1.8 Maintenance preparation and training

Prior to and during commissioning the maintenance engineer should set up the appropriate maintenance systems and documentation. Each major item of equipment should be given an identification code, which should be marked on the equipment itself.

The maintenance manuals for the equipment should be obtained from the manufacturer and reviewed. Sometimes the manuals will be considered inadequate in some respect. If so, the manufacturer should be contacted concerning modification. More often, however, problems arise because the manuals have not been consulted.

The maintenance of the equipment, both preventive and breakdown maintenance, should be planned. Schedules for regular preventive maintenance should be drawn up. A system of maintenance records should be instituted, containing details of the equipment in the plant and of the maintenance and modification work done. Details of the records required for pressure vessels, for example, are given in Section 19.3, but the records should not be limited to such equipment. The quality of the data available for analysis for reliability, availability and maintenance of the plant depends critically on these records. It is far easier to create an effective system initially than to try to improve a defective one. It is particularly important to obtain good

information on the symptoms and causes of faults, and on the action taken.

A system of spares holdings should be created. Important features of such a system are that it show clearly what spares are available, what spares are being consumed and what the delivery situations are. Only if this information is available is it possible to make rational decisions on the spares holdings.

A system for the control of slip plates should be devised so as to ensure that at each stage, such as normal operation or shut-down, all the slip plates required, but no others, are in position. The system should include provisions to prevent confusion with contractors' slip plates.

Maintenance personnel should check the plant during construction for accessibility and ease of maintenance. It may be necessary to make some alterations to the layout, to the equipment or to the lifting arrangements. The maintenance function is also involved in many of the pre-start-up activities such as checking and testing, and suitable preparations need to be made for this.

Maintenance personnel typically serve a number of plants and generally receive only limited instruction in respect of a particular plant, but they do need to be trained in the hazards of the materials, in the alarms and emergency procedures and in the maintenance of equipment specific to the plant. This may include some training at the vendor's works.

19.1.9 Pre-commissioning documentation

It is difficult to overemphasize the importance of having a comprehensive and up-to-date set of documentation. The documentation as a critical feature of the management system was described in detail in Chapter 6.

It is appropriate here, therefore, only to re-emphasize certain aspects which are of particular importance in commissioning. The documentation available at the pre-commissioning stage should include:

(1) operating manual;
(2) operating instructions;
(3) safety instructions;
(4) permit system documents;
(5) pressure vessel register;
(6) pressure piping systems register;
(7) protective device register;
(8) maintenance systems and documents;
(9) checklists.

The plant should be covered by a comprehensive system of permits-to-work as described in Chapter 21. These are needed during the commissioning as much as during operation and should be developed in good time.

The registers for pressure vessels, pressure piping systems and protective devices should be etablished before commissioning. Details of individual items can then be entered as they are installed and examined. The registers are described more fully in Sections 19.3 and 19.4.

There are several systems of documentation required for maintenance, as already described.

A major part of commissioning is the checking of systems, both of hardware and of software. This is greatly assisted if suitable checklists have been prepared.

19.1.10 Modification control

There should be a system for the control of modifications during commissioning, as described in Chapter 21, so as to ensure that a safe design is not rendered unsafe by a modification. The system should ensure that proposed changes are identified and routed to the design authority and that there is a prompt response.

There should be a single channel through which modifications are communicated to the contractor, so that there is less risk of confusion. On a large project this may require the appointment of a commissioning modifications engineer.

Any modification arising from the commissioning should be referred for examination by a hazard and operability (hazop) study in a manner akin to that pertaining during design and using similar criteria to decide whether such a study is necessary.

A modification proposed may be to an existing plant rather than to the plant or plant section being commissioned, in which case there will be additional matters to allow for. A major consideration is whether the modification is to be done during a plant shut-down or with the plant in operation. In either case it is necessary to take account of the hazards, to see that the plant is in a stable operating condition and to ensure that contractors are aware of the hazards.

19.1.11 Mechanical completion and pre-commissioning

A particular aspect of pre-commissioning is mechanical completion. The term is applied to individual items of equipment and is used to cover the activities between installation and process commissioning.

Mechanical completion ensures that the installed equipment is ready for commissioning and involves checking that it is installed correctly, that the component parts operate as specified and that any ancillary equipment is installed and working. Some typical checks and tests carried out on process equipment and machinery are listed in Table 19.4.

The plant should be given a thorough visual inspection. A check should be made on all plant equipment and pipework to ensure that it is installed in accordance with the engineering drawings. Any discrepancies should be marked on drawings to show the 'as built' condition. These discrepancies should be reviewed and corrected if necessary. In one instance, for example, a safety shower was found to contain not water but caustic soda. The inspection should check for items such as loose bolts or missing valve wheels and for construction aids or debris left in the plant.

The plant layout should be checked with respect to features such as: means of access and escape routes; floors, stairs and handrails; lighting; fire equipment; and safety equipment.

Mechanical equipment should conform to the specified codes and standards, should be installed in accordance with the relevant drawings and should meet the performance tests specified.

Each item of equipment received should be checked for compliance with specification. In some cases this may mean witnessing aspects such as examination or testing at the manufacturer's works.

Errors in the materials of construction actually installed are quite common. A check should be made, therefore, on the materials. In critical applications it may

Table 19.4 *Some checks and tests carried out on process equipment and machinery during plant commissioning*

Pre-installation inspection, checking and testing of:
pressure vessels
process machinery
Plant checking against piping and instrument diagram
Checks on materials of construction
Pressure vessel and system tests:
inspection
pressure tests
leak tests
protective devices tests
Process machinery tests:
inspection
dry runs
load runs
performance runs
Subsystem and system tests:
dynamic safe fluid test (water test)
dynamic process fluid test
Also tests on:
utilities
instrumentation
unit operations
simulated faults

be appropriate to carry out a 100% check using a device such as a Metascope.

The installation of internal fittings, such as trays, weirs, downcomers and thermocouple pockets in distillation columns, should be checked. It is important that these internal fittings have the right dimensions, are correctly located and are firmly secured.

For rotating equipment checks are required on foundations, lubrication systems, other ancillary systems, alignment and vibration-related features.

Piping systems should be checked for: conformity with pipework isometric and other drawings; the presence of fittings such as isolation valves, drain and sample points, etc; the orientation of fittings such as non-return valves, where applicable; satisfactory making of joints; adequate pipework supports; and for satisfactory installation of expansion joints and bellows. A test sheet for piping systems given by Horsley and Parkison is shown in Table 19.5. Much use is made of checklists in assuring mechanical completion. Many of the checklists given in Table 19.2 apply to this phase.

For virtually all the features mentioned there are associated documents and/or drawings. The process of checking involves the marking up of drawings and the completion of test certificates and various forms of contractual certificate.

There are also a number of pre-commissioning activities to be carried out on the mechanical systems. These activities need to be coordinated both with the site construction manager and with the plant operations and maintenance management.

Typically the pre-commissioning activities include: first, commissioning of the utilities so that services are available; checks on the individual equipments and systems for mechanical completeness and listing of missing items; pressure tests on pressure vessels and defined pressure piping systems; cleaning of vessels and flushing out of pipework; loading in of catalysts and packings; and leak testing.

The inspection and testing of pressure vessels is described in Section 19.3.

At the same time, rotating machinery is run off-load and instrumentation is set up, calibrated and given functional tests.

A list of some of the checks and tests carried out on process machinery such as pumps, compressors and centrifuges, is given in Table 19.6.

It is common practice to fit start-up filters on rotating equipment to protect it from debris which could cause damage. Sensitive instrumentation which could be damaged is also temporarily removed.

Subsystems are frequently tested using a safe medium, usually air or water, prior to testing with the process fluid. Compressors may be run on air on open circuit, and pumps may be run on water.

19.1.12 Control systems

The installation of the instrument and control system cannot be completed until most of the mechanical equipment is installed. Its installation tends to overlap with the commissioning of the rest of the plant.

Guidance on the installation and testing of instrument and control systems is given in BS 6739: 1986 *Code of Practice for Instrumentation in Process Control Systems: Installation Design and Practice*.

Most control systems are now based on some form of computer control, and this is assumed in the account given here. The computer is first tested at the supplier's works. These tests cover the computer hardware, the input/output equipment, and any non-standard software. The functions to be performed through the configurable software are entered, such as signal conditioning, trend records, overview displays, alarms, control algorithms, etc., and are then tested. Likewise, applications software for functions such as sequential control or fault diagnosis is entered and tested.

Table 19.6 shows some of the checks carried out on instruments. A check should be made that the instrument is installed in accordance with the drawings and with the manufacturer's instructions. It should also be checked that shipping restrictions have been removed. Usually parts and springs are wired down, critical parts are covered with protective coating and leads may be plugged; all these restrictions need to be taken out.

Installation of the instrumentation is followed by checking. The responsibility for this normally lies with the contractor, but involvement of the user's instrument personnel assists familiarization.

Circuits should be checked for continuity from the panel to the instrument, and back. The movement of a control valve should be checked by 'stroking' it and that of a controller by observing its response to the output of the measuring element. The response of the alarms and interlocks to the measuring elements should be checked, as should the alarm settings and the actions of devices actuated by the interlocks. Similar checks should be made on trip systems.

Instrumentation received will have been calibrated by the manufacturer but some degree of recalibration on site may be required, whether as a result of damage

Table 19.5 *Typical pressure piping test sheet (Horsley and Parkinson, 1990) (Courtesy of the Institution of Chemical Engineers)*

Design and Test Data		
Availability of the following data relevant to the piping system	Engineering line diagram	
	Piping test schedule	
	Piping arrangement drawing	
	Pipe, line schedule	
	Piping and valve specifications	
	Piping isometrics	
	Piping test procedure	
	Piping fabrication and erection codes	
	Pipe support details and schedule	
Test certificates for	Off-site fabricated piping	
	Heat treatment or other	
	Process/Utility valves, control valves etc.	
	NDT (X- or γ-ray, etc.)	
	In-line process equipment	
Piping and valve material analysis certificates		
Welders qualification certificates		
Pre-test Visual Inspection		
Routing and size correct to ELD arrangement drawing/piping isometric		
Installation of piping and piping components complete	Joints bolts nuts and gaskets expansion loops and bellows	
	Fixed anchors, sliding supports, guides spring or fixed hangers	
	Jackets/jumpers, tracing conductive bolts/earthing straps	
Installation/ orientation with respect to flow	Process and utility valves, NR valves process control valves orifice plates and flowmeters	
Location of in line components for access, operation maintenance and safety of operatives		
Location and installation of	Vents, drains, drip legs, drip rings, utility station connections, steam traps, filters, strainers line blinds, spectacle plates, bypasses, instrument tapping points for pressure, temperature and flow, plugs, rodding out points	
Installation of field mounted instruments, i.e. Thermowells, pressure gauges, etc.		
Check and ensure system devoid of insulation and paint		

Pre-test Preparation		
Prepare a written test plan and mark ELD/GA with location of all spools, spades, blanks, vent valves, strainers, etc., agree with site manager and initiate		
Obtain spades, blanks, strainers, vent valves, bolts, nuts, gaskets and fabricate pipe spools		
Remove RVs for bench testing and orifice plates for checking, make good joints or blank off		
Remove or spade off any control valve or instrument liable to damage under test pressure, replace with spool or make good joint and open any bypass valves		
Spade off or isolate process equipment with lower allowable pressure than test pressure		
Spade off all overflows, close drains, fit vent valves, ensure test medium available		
Calibrate test gauge and check range adequate for test pressure and detect pressure loss		
Define testing fluid		
Pressure Test Procedure		
Site manager's clearance obtained, other contractors informed and safety notices positioned		
Ensure all test personnel are competent and briefed regarding extent, duration and limits of test		
Open up system, flush or blow through to remove mill scale/rubbish, fit temporary strainers and close		
Hook up test pump to line and test medium, open vents and commence filling system		
Conduct test per test procedure, attend to remedial works and bring to test pressure and hold		
Invite client's representative to witness test		
Prepare test certificate and record	System title, line numbers, plant reference	
	Numbers, date, time and duration of test	
	Pressure, test certificate number and obtain client's signature	
Post-test Procedure		
Open up, drain down, remove and account for all spades, blanks, spools, plugs, vent valves, strainers and test equipment, flush or blow through and dry out		
With new gaskets, re-install at bench tested RVs, orifice plates, control valves, thermowells, flowmeters, pressure gauges and remove safety notices, etc.		
Check installation complete and purge or chemically clean if part of take-over procedure		
Complete construction works, e.g. paint, insulate, colour code, etc.		

ELD, engineering line diagram; GA, general arrangement; NDT, non-destructive testing; NR, non-return; RV, relief valve

Table 19.6 *Some elements of the checking and testing of process machinery and instruments (after Gans and Benge, 1974) (Courtesy of the Institution of Chemical Engineers)*

Process machinery:
Field disassembly and reassembly
Lubrication system: cleaning and check on circulation (flow, temperature)
Cooling water system: cleaning and check on circulation (flow, temperature)
Pre-commissioning of instruments
Check on free and unhindered rotation
Check on anchor bolts
Disconnection of piping to check that it does not stress equipment
Installation of temporary filter
Setting of system for 'no load' running
Running of motor uncoupled
Coupling of motor
Check on alignment
Check on vent system
Check on seal system
Dry run: check on vibrations and overheating of bearings
Load run
Performance run
Instruments:
Instrument checking against drawings and manufacturer's requirements
Removal of shipping restrictions
Calibration
Continuity check
Movement check
Alarms check
Interlocks check
Analysers check

sustained or as a matter of policy, and this necessitates appropriate test equipment.

These checks are then followed by functional testing. Some functions are commonly executed by the main, computer-based system and some by separate systems.

Early installation of the computer system allows progress to be made with the testing of the instrumentation connected to it and of the functions allocated to it, in particular of non-standard systems software, configurable software and applications software.

Some common functions which are often separate from the computer system are (1) management information, (2) specialized instruments, (3) packaged units, (4) control loops, (5) trips, (6) sequence control, (7) emergency shut-down and (8) stand-by supplies.

Checklists for the functional testing of a control loop and of a sequence are given by Horsley and Parkinson (1990). The headings of the checklist for a control loop are (1) input channel, (2) faceplate/bar display, (3) trend display, (4) archiving, (5) alarm handling, (6) control functions, (7) output channel and (8) documentation. Those for a sequence are (1) declarations, (2) structure, (3) timing, (4) contention handling, (5) operator access, (6) recovery options, (7) recipe handling, (8) firmware interface, (9) sequence display and (10) batch logging.

The pre-commissioning of the control system should be governed by formal procedures. Test forms should be specified for each system to be tested. Guidance and model forms are given in BS 6739: 1986.

Proposals for modification to functional specifications or to the computer software should be referred for review by a hazop study in a manner similar to that pertaining in design. There should be a formal system to ensure that changes made to the computer software are recorded and that development of the software proceeds by way of discrete, identifiable and documented versions.

It is necessary to ensure by formal means that the segregation of signals is not compromised by modification. Segregation of signals may be according to signal type, plant area and, process function, and has implications for features such as intrinsic safety, electrical isolation and emergency shut-down.

Formal control should be exercised over access to the computer system. Parties requiring access are control engineers comissioning the control system and process engineers commissioning the plant. Levels of access should be defined and controlled by means such as passwords or key switches.

The checks on the instrumentation should be extended where practical to cover operation with process fluids and conditions which are realistic but nevertheless safe.

Documentation for the instrument and control system should include: the system manuals; piping and instrument diagram; loop diagrams; wiring/circuit diagrams; termination rack layouts; tag number lists; database tables; sequence flow diagrams; etc.

19.1.13 Process commissioning

Process commissioning is begun only when the pre-commissioning is complete and the defects identified have been corrected to the extent judged necessary. This commissioning may be undertaken on equipments or sections of plant as they become available, but only under close control so as to prevent hazardous interaction between the two activities of plant construction and process operation. One method of control is to require for the equipment a formal handover certificate verifying mechanical completion, with minor deficiencies listed. Before the process commissioning starts, it is usual to carry out a final check. Checklists applicable at this stage are one of those most commonly given.

The order in which the process commissioning is done may vary. The typical sequence cited by Horsley and Parkinson (1990) is (1) utilities, (2) laboratory, (3) raw material storage, (4) ancillary equipment, (5) reaction system, (6) work-up system and (7) product storage. Where there is no reaction system, the overall process system may be substituted for stages (5) and (6).

The quality control laboratory needs to be in a position to take samples from the plant and conduct analyses as specified. If there is any deficiency in its ability to do this which is sufficiently serious, commissioning should not be started. The laboratory needs also to be prepared to handle the augmented number of analyses likely to be required during the commissioning period.

Ancillary equipment can often be commissioned separately from the equipment which it serves. Where this is possible, it is prudent to do this, so that when commissioning of the main equipment is begun, the ancillary equipment is ready for use.

A supply of raw materials is necessary for the process commissioning. These may come from a bulk storage or

from other containments such as drums or transportable containers. Bulk raw materials storage will normally be commissioned some time in advance. It is also necessary to commission the intermediates and products storage, which is generally bulk storage. A checklist for the commissioning of a storage tank is referenced in Table 19.2.

The reaction section may be continuous or batch. Since this section is generally a critical one, its commissioning should be prepared with particular care. The commissioning team should be at full strength and fresh.

For a continuous reactor the commissioning will aim to start up and achieve a steady state as smoothly as possible. Critical features in achieving this are the utilities, the feeds, the machinery and the control system. A checklist for the commissioning of a continous reactor is referenced in Table 19.2.

It may well happen that the conditions obtained are not those desired or that some fault occurs and the product produced is off specification. Horsley and Parkinson advise that, provided it is safe to do so, it may be better to continue running until it is established that the desired product quality can be made before shutting down, thus avoiding repetition of start-up and shut-down.

For a batch reactor the problems are rather different. Here the requirement is to ensure that correct charges are made, that the desired sequence is followed, and that at each stage the process is controlled as specified. Critical features in this case are the charging, the control system for the sequences and the process conditions.

For both types of reactor a full record of the trials should be kept to allow the design to be checked and any deficiencies experienced corrected.

19.1.14 Handover: contractor project

The conditions for acceptance of the plant from the constructor by the operator are normally specified in the contract. A handover certificate is usually issued which contains a list of reservations of items on which further work is required. The handover needs to be carried out formally and with particular regard to safety. The plant should be in a safe condition when it is handed over.

With a large plant it may be desirable to have selective handover of plant systems as they are completed. This applies particularly to such systems as steam-raising plant, steam pipework and cooling water systems.

If parts of the plant are to be operated while other plants are still under construction, it is essential to take steps to ensure that these two activities do not interact in such a way as to create a hazard. The problem is similar to that arising in a major plant extension, and this is discussed in Chapter 21.

A typical reservations checklist is given by L. Pearson (1977b) and is shown in Table 19.7. The checklist referenced in Table 19.2 is similar.

19.1.15 Start-up and performance testing

With the end of the process commissioning, the next stage is to charge the feedstocks and start up and operate the whole plant and subject it to performance testing in order to determine whether it meets its specification. This initial start-up of the plant should be thoroughly prepared. It should be recognized that the start-up may be prolonged and arrangements made to relieve personnel so that they do not have to work excessively long hours. It is valuable to keep fairly comprehensive records of the start-up, and personnel should be briefed on the recording requirements.

All the formal systems for control of hazards and errors should be operational. These include in particular the permit-to-work systems as well as the systems for the control of slip plates and of vents and drains.

Before start-up a careful check should be made by 'walking the plant'. The inspection should include a check on the state of all valves, which may be assisted by use of marked drawings and a register. Likewise, a check is required to ensure that all sliplates which need to be removed have been removed; again this can be done, using drawings and a register.

It may be necessary during start-up to use filling and bypass lines which need to be closed again when the plant is operating. A register of such lines is needed to ensure that this action is taken.

The disarming of certain trips may also be necessary during start-up, particularly those for low flow, pressure and temperature. There should be a formal system to cover this which ensures that such disarming occurs only as authorized and that the instruments are restored again when the need for disarming has passed.

Checklists given by L. Pearson (1977b) of measures to be taken before process fluids are admitted are given in Table 19.7. The checklists referenced in Table 19.2 are similar. Start up procedures are described further in Chapter 20.

The purpose of performance testing is to confirm that the plant can be operated at design conditions and that with a specified raw materials quality and at these conditions it will perform to specification in respect of throughput, yield and product quality. There may also be specifications for features such as utility usage, effluent quantities and compositions, and reliability. A schedule of performance tests will have been drawn up and the levels of performance which the plant must meet specified.

The feedstocks are charged to the plant and it is started up and operated to determine whether it meets these performance criteria. The outcome of the performance testing may be: (1) that the plant performs satisfactorily; (2) that the plant does not perform satisfactorily and there is minimal prospect that it ever will; or (3) that the performance of the plant, whilst falling short of specification, can be remedied. In case (3) the contractor may either put the matter right at his own expense or agree compensation with the client, whilst in case (2) the contractor has a financial liability.

19.1.16 Handover: in-house project

For a turn-key contract, the system of formal handover sets a term to the commissioning period. For an in-house project the possibility exists that the commissioning period will become unduly extended.

The commissioning period should not be terminated until the plant is giving reasonably satisfactory operation. The rate of improvement inevitably slows down when the additional support of the special commissioning team is withdrawn. On the other hand, the development of a plant is a continuing process and the commissioning cannot be allowed to drag on indefinitely.

Table 19.7 *Checklists of measures to be taken before process fluids are admitted on a chemical plant (L. Pearson, 1977b) (Courtesy of Hydrocarbon Processing)*

(a) Pipelines and pipework checklist

1 Screwed plugs in pipes, only permissible on air, water, nitrogen under 100 psi, $1\frac{1}{2}$ in. NB and below
2 Faulty welding
3 Correct joints
4 Odd sized bolts
5 Black bolts in cold joints
6 Faulty pipeline supports
7 Pipe not resting on supports
8 Are expansion slippers safe (e.g. will they push off structure when line is hot?)
9 Check spring hanger settings
10 Faulty spring hangers
11 Low point drains fitted where necessary, and high point vents
12 Lagging – missing, damaged, loose, etc.
13 Vent and drain blanks fitted where necessary
14 'Weep holes' in relief valve exhaust lines, only on non-H/C or atmospheric. RVs
15 Have all slip plates been removed and spectacle plates turned?
16 Spring hangers – have restraining pins been removed?
17 Make sure pipework is up to the piping and instrument diagram specification
18 Necking-off hazard – is there any equipment or small bore pipe projection that can be accidentally broken off?
19 Are small branches, i.e. drains, sufficiently clear of pipe supports?
20 Do drain lines run to underground drains? They should not flow over paved areas
21 Flanges lagged up

(b) 'Chemicals and hydrocarbons in' checklist (jobs to be done before chemicals or hydrocarbons can be safely brought into the plant)

Complete all necessary reservations
Nitrogen purge systems prepared and leak tested
Blowdown system 'live'
Oil/water separator in commission
New perimeter fence erected, with 'dematched area' notices
Dematching hut in position and gateman available
Brief all construction people on consequence of plant becoming a 'dematched area'
Fire alarm I/C and all positions tested
Compressed air sets in position
Fire extinguishers in position
Eye wash bottles in position
Personnel showers in position and checked
Fire hoses in position
Fire main I/C and check that hoses fit hydrants
Drench water sprays tested
Fire steam hoses in position and check they connect securely
Fire permits in use
Flush drains to prove them free from obstructions
Plant areas clean (fire hazards removed – rags, paper, wood, etc.)
Check plant lighting
Remove contractors' buildings, tarpaulins, etc.
Remove non-flameproof equipment
Nominate shift fire teams and arrange practice alarm
List all possible welding jobs – get most done beforehand
Check that welding sets pass works electrical inspection
Check gas detectors
Hazard and safety notices to be in position
Obtain 'means of escape' certificate
Check that segregation plates can be easily removed
Inform fire station
Invite safety department to inspect and pass comment
Carry out thorough search for matches
Make sure that neighbouring plants know how this affects them
Inform services (affect their drains)
Inform Factory Inspector and Alkali Inspector
Inform local authorities
Inform records section

H/C, hydrocarbon; I/C, in commission; NB, nominal bore; RV, relief valve

Some criteria for termination are given by Kinglsey, Kneale and Schwartz (1968–69) as follows: (1) competence of operating staff; (2) reasonable level of plant reliability; (3) attainment of acceptable quality standards; (4) satisfactory use of resources (staff, materials, utilities, throughput); and (5) acceptable level of maintenance.

19.1.17 Safety audit

The plant should be given a comprehensive safety audit during the commissioning period. The audit should cover both hardware and software aspects. Details of such a safety audit have been given in Chapter 8.

19.1.18 Commissioning problems

Many of the problems associated with commissioning have been mentioned explicitly or are implicit in the comments made, but it is appropriate at this point to give a further review of some of the problem areas in commissioning. These include:

(1) lack of process information;
(2) design changes;
(3) unsuitable equipment;
(4) lack of expert advice;
(5) lack of spares and supplies;
(6) construction and maintenance errors;

(7) safe fluid testing;
(8) water traces;
(9) operating errors.

The difficulties inherent in a situation where basic information about the process is inadequate have already been mentioned. This is due sometimes, but by no means always, to the purchase of knowhow from outside.

Although some modifications of the original design are almost inevitable, they tend to be disruptive and expensive, and should be kept to a minimum.

Unsuitable equipment can be a source of much trouble. It is sometimes suggested that equipment which comes as a package unit or is purchased from the main contractor can be troublesome. It may well be, however, that in many cases the problem lies with the user. Certainly it is essential that he give as full a specification for such equipment as for other items.

The need for expert advice has already been mentioned. The behaviour of equipment during the running-in period may be different from that in normal operation. In one case, for example, commissioning was delayed because the lubricating oil from the bearing of a ball mill was found to contain a high concentration of metal particles: the vendor then confirmed that this was normal during running-in.

Shortages of spares and other materials can result in delays. The need for an adequate spares system has already been emphasized, but provision of other items is equally important.

Mistakes in construction are commonplace. In addition to the use of incorrect materials of construction for the main equipments and pipework, errors often occur in minor items such as bolts or gaskets. For example, mild steel bolts may be fitted where stainless steel bolts have been specified, which in a low temperature application is a serious hazard. Likewise, a hazard can be introduced by the use of a wrong gasket.

Safe fluid testing can sometimes introduce its own problems. The use of water instead of a hydrocarbon means that the weight of the fluid is greater. There may be a risk of overpressuring the base of tall columns or of overstressing vessel supports.

Likewise, it is not unknown for damage to be done to compressor systems by an air inlet line choked by polyethylene bags.

Certain plants, notably cryogenic plants, are sensitive to even small quantities of water. Ice and hydrates can cause numerous problems, particularly on instrumentation. It may be necessary to remove water by blowing through the drains and by a warm air purge of the plant.

Inexperience on the part of the process operators can result in maloperation which does considerable damage to the plant. For example, a pump may be allowed to run dry or to pump against a closed valve.

Operation of equipment at higher temperatures than intended so that the creep rate is greatly increased can be particularly serious. It is quite possible to use up a large proportion of the creep life, say 30%, during the commissioning. It is important, therefore, that this be avoided as far as possible and that the records kept be such as to allow an estimate of creep effects during commissioning to be made.

Some specific problems arising during commissioning have been reviewed by Kingsley, Kneale and Schwartz (1968–69) and are summarized in Table 19.8. Design errors do occur, but are most frequent in detailed rather than fundamental aspects. Emulsions and foams may occur on the full-scale plant, even though these have not shown up in the pilot plant. Gas phase balancing errors can lead to difficulties with levels and flows. Lack of a net positive suction head causes pumps to cavitate. Heat transfer phenomena which can be troublesome include polymerization and scaling-up. The former occurs more frequently than is admitted. Separation operations, especially those involving particulate systems, give rise to many difficulties.

Automatic control problems include measurement of unusual variables, the oversizing of control valves and the control of non-linear variables and of loops with large time lags and/or dead time.

Table 19.8 *Some typical problems arising during plant commissioning (after Kingsley, Kneale and Schwartz, 1968–69) (Courtesy of the Institution of Mechanical Engineers)*

Design errors:
emulsions and foams
venting arrangements
liquid head arrangements
Heat transfer phenomena:
polymerization
scaling up
Separation operations:
liquid–liquid separation, e.g. centrifuges
liquid–solid separation, e.g. filtration
gas–liquid separation, e.g. demisting
gas–solid separation, e.g. gas filtration
Automatic control:
long time lags, dead time
valve sizing
control of nonlinear variables, e.g. pH
unusual measurements
Unsuitable equipment
Leaks:
sudden leaks
leaks in vacuum equipment
Vibration phenomena
Mounting errors
Mechanical handling equipment
Materials of construction

19.1.19 Commissioning hazards

The process and plant designs should already have been subjected to the various checks described in Chapter 8. In particular, the hazop study conducted should have covered operations which are carried out only in commissioning. There are certain specific hazards associated with commissioning.

The pressure testing of equipment, which is described in Section 19.7, is a hazardous operation. The hazard is minimized by the use of hydraulic rather than pneumatic testing, but the energy released if the vessel fails is appreciable even with a hydraulic test, and it is important to ensure that the correct test procedure is followed and

that personnel not involved in the test are cleared from the area.

Many of the test and other operations carried out during commissioning require the use of temporary connections. These are often hoses. Hose connections have been responsible for many accidents and particular care should be exercised with them.

Plant are tested for leaks, but, even so, leaks tend to develop due to features such as loose joints, open valves, gasket and seal failures, vibration, thermal expansion and contraction, and corrosion. It is important, therefore, to keep a lookout for such leaks. Leaks from high pressure plant can cause direct injury to personnel, leaks of flammable materials can cause a fire or explosion and leaks of flammable liquids can contaminate lagging, creating a further fire hazard.

Nitrogen purging is a frequent operation in commissioning. The use of nitrogen for large-scale purging operations involves the hazard of asphyxiation of personnel.

Commissioning requires the use of utilities in large quantities. It is important to ensure that other plants are not run short of essential utilities and so put at risk. There is the further hazard of contamination of the utilities by fluids from the plant being commissioned.

19.1.20 Post-commissioning documentation

During the commissioning a large amount of information is generated which needs to be properly documented. Modifications are made to the plant; a wide variety of tests and examinations are performed on individual items of equipment and on the plant as a whole; the computer software is modified and parameters entered; modifications are made to the systems and procedures and the associated documentation; reviews are made of safety and environmental features; and there are matters to be carried forward.

Some principal features of the post-commissioning documentation are:

(1) modifications records;
(2) equipment examination records –
  (a) pressure vessels,
  (b) pressure piping,
  (c) protective devices;
(3) equipment test records –
  (a) pressure and leak tests,
  (b) pressure relief valve tests,
  (c) rotating machinery tests,
  (d) instrument tests,
  (e) computer system tests,
(4) computer records;
(5) spare inventories;
(6) safety reviews records –
  (a) hazop follow-up;
  (b) safety audit;
(7) environmental review records;
(8) reservation list.

There should be records of any modifications made to the plant and also to the process. This aspect has already been discussed.

The registers for the pressure vessels, pressure piping sytems and protective devices should have been prepared prior to commissioning, but much information on the equipment and on its initial examination and testing will be entered at the commissioning stage.

Records should be kept of the tests done on the whole range of equipment, including pressure vessels and the pressure piping system, pressure relief valves, rotating machinery, instruments and the computer system. Any modifications made to the computer software or to the parameters entered should be recorded.

It is common practice to hold an inventory of commissioning spares. With the end of commissioning this should be replaced by the regular spares inventory, which should be documented.

There should be records of any safety and environmental reviews conducted. The safety reviews should include any matters requiring follow-up consequent on the main hazop study or any further hazop studies performed as a result of commissioning modification and the post-commissioning safety audit.

There will also have been modifications made to the various types of documentation such as operating instructions, test procedures, etc., and these changes should now be incorporated and tidy documents produced.

19.2 Plant Inspection

Plant inspection is an essential aspect of the fabrication, construction, commissioning and operation of pressure systems. Accounts of plant inspection are given in *Pressure Vessel Systems* (Kohan, 1987) and *Inspection of Industrial Plant* (Pilborough, 1989) and by Erskine (1980).

Relevant codes are the *Pressure Vessel Examination Code* (IP, 1993 MCSP Pt 12) and the *Pressure Piping Systems Examination Code* (IP, 1993 MCSP Pt 13). These are codes with international application but are aligned with the Pressure Systems and Transportable Gas Containers Regulations 1989.

Another code is the *Registration and Periodic Inspection of Pressure Vessels Code* (ICI/RoSPSA 1975 IS/107) (the ICI *Pressure Vessel Inspection Code*). This is now out of print but remains a good illustration of the fundamental principles of such codes.

In the USA, the *Guide for Inspection of Refinery Equipment* by the API (1962–) has long been a principal inspection code but is now out of print. The *Guide* has some 20 chapters which are listed in Appendix 27. It is being replaced by other publications. One of these is API RP 510: 1989 *Pressure Vessel Inspection Code: Inspection, Rating, Repair and Alteration*.

The following description is concerned mainly with the inspection of pressure vessels, pipework and protective devices, but it illustrates general principles for inspection which are relevant also to many other types of equipment.

Selected references on plant inspection, testing and monitoring are given in Table 19.9.

19.2.1 Regulatory requirements

The statutory requirements for inspection of pressure vessels and the legislative background to these were described in Chapter 3. The basic position in the UK is that until 1989 there were statutory requirements covering the construction and maintenance, including inspection of steam boilers and receivers, air receivers,

Table 19.9 *Selected references on plant inspection, testing and monitoring*

API (Appendix 27, 1967– Refinery Inspection Guide, 1984 Publ. 2002, 2004, 1990 RP 574, 1991 RP 573, 1992 RP 510, 572); NRC (Appendix 28 *Inspection*); Welding Institute (Appendix 27, 28); BCISC (1959/3); Honeyman (1960); Barnhart (1963); Kirchner (1967); ASME (1979– *Pressure Piping Code*, 1992 *Boiler and Pressure Vessel Inspection Code*); Ministry of Technology (1969a); Kobrin (1970); Pilborough (1971, 1989); Welding Institute (1972 Item 22); M.J. Neale (1974, 1980); Collacott (1975, 1976a,b, 1977a,b, 1985); ICI/RoSPA (1975 IS/107); IMechE (1975/18); Dickenson (1976); Edeleanu (1976, 1981); Fromme (1976); IChemE (1976/63); IP (1976, 1993 MCSP Pt 12, 14); R. James and Bloch (1976); Harvey (1976, 1979b); R. Morris (1976); Filetti and Trumpler (1977); National Vulcan (1977); R.L. Clark (1978); Himmelblau (1978); HSE (1978b); R. King and Magid (1979); Czaga and Drury (1981); Kister (1981b); Marre and Reichert (1979); Sims (1980); London (1982); Anon. (1983f); Wamsley (1983); Coley (1985); Chowdhury (1986); Erskine (1986); Conroy (1987); Krisher (1987); R.L. White (1987); Plant Safety Ltd (1990); Depue (1991); Witherill (1991)
BS (Appendix 27 Test Methods), BS 5500: 1991

Fault diagnosis
Pau (1975, 1981a,b); R. Morris (1976); Anon. (1977 LPB 14, p. 17); Chamberlain (1980); Schweitzer (1982); Edgar *et al.* (1984); M.W.J. Lewis (1984); Marney and Foord (1984); M.J. Lewis (1993)

Pressure vessels, piping, fittings
Gibbs and White (1961); Buhrow (1971); O'Neill and Jordan (1972); Toogood (1972); Whenray (1972); Lautzenheiser (1974); ICI/RoSPA (1975 IS/107); Dunt (1976); Erskine (1976b, 1980); Kussmaul, Blind and Ewald (1977); Ludwig (1978); IP (1979); Nichols (1979b); Jessop (1980); Kussmaul *et al.* (1980); McDermod (1982); Baker-Counsell (1985f); Guth and Clark (1985); Tayler (1985c); Burke and Moore (1990); K.P. Singh (1990); IMechE (1991/132, 1993/154)
BS 3889: 1966–, BS 470: 1984
Columns: Bowman (1991)

Tanks
Truscott and Livingstone (1978); Hallan (1994)

Glass equipment
Lofberg (1965)

Paints
Berger (1983)

Rotating machinery
Sela (1978); E.R. Bowen, Rotondi and Reid (1980); Finley (1980); B.R. Singh and Thomas (1980); Godse (1990, 1991); R.F. Wong (1992)

Pipelines
AGA (Appendix 28); British Gas (Appendix 27 *Commissioning and On Line Inspection*, 1989 Comm. 1409); Holm (1984); Clerehugh, Shannon and Jackson (1983); Braithwaite (1985); Gordon, Murphy and Dean (1985); L. Jackson, Shannon and Adley (1985); Jamieson (1985); Watanabe and Himmelblau (1986); IGasE (1987 IGE/SR/10); Weisweiler and Sergeev (1987); Ellul (1989); Clerehugh (1991); Stouffs and Giot (1993)
Pipeline location detection: British Gas (1987 Comm. 1345, 1989 Comm. 1410)

Ammonia plants
Truscott and Livingstone (1978); Madhavan and Sathe (1987); Prasek (1988); Burke and Moore (1990)

Test procedures
Shaw, Sykes and Ormsby (1980); British Gas (1986 Comm. 1305); G.J. Gibson (1987); ASME (1991 PTC1–1991)
Structures: Collacott (1985)
Steam plant: ASME (1980 PTC 39.1–1980); van Kapel (1990)
Centrifuges: AIChE (1980 E-21)
Driers, including spray driers: AIChE (1985 E-23, 1988 E-26)
Mixers: AIChE (1965 E-7, 1986 E-25)
Pressure vessels: API (1967– *Refinery Inspection Guide*, 1992 RP 510, 572); T.E. Taylor (1968–69); ASME (1992 *Boiler and Pressure Vessel Code*)
Distillation columns: AIChE (1962 E-10, 1986 E-24)
Heat exchangers: AIChE (E-15)
Tanks: Truscott and Livingstone (1978); Briggs, Richards and Fiesinger (1986)
Pipelines: British Gas (Appendix 27 *Testing*); ASME (1979– *Pressure Piping Code*); API (1991 RP 1110)
Welds: Bartholomé and Vasoukis (1975); Eisenberg (1975)
Steam traps: ASME (1980 PTC 39.1)
Valves: API (1992 RP 574); BS 6755: 1986–
Fired heaters: AIChE (1977 E-16, 1989 E-27); API (1991 RP 573)
Steam turbines: ASME (1976 PTC 6–1976)
Compressors: ASME (1974 PTC 10–1974); BS 1571: 1975, BS 3122: 1990–
Pumps: AIChE (E-5, 1968 E-14, 1984 E-22), Shull and Church (1991), BS 599: 1966, BS 5316: 1976–
Fans: BS 848: 1980
Pressure relief devices: API (1960 RP 525, 1974 *Refinery Inspection Guide* Pt 16, 1992 RP 575); ASME (1988 PTC 25.3–1988)
Incinerators: ASME (1978 PTC 33)
Other process equipment: AIChE (1977 E-18, 1978 E-19, 1980 E-20)
Fire protection equipment: MCA (SG-13); P. Nash (1975b,c); R. Phillips (1981); NFPA (1994/41)

Visual inspection
Pilborough (1971, 1989); Elliott (1976); Keymed Industrial (1983); Dooner (1986)

Pressure testing
Ferge (1972); Anon. (1979 LPB 26, p. 39); Hearfield (1980b); AGA (1981/36, 1984/40); Kiefner and Forte (1985); Anon. (1986 LPB 72, p. 7); Kletz (1987d); Gwynn (1988); Dooner and Marshall (1989 LPB 86); HSE (1992 GS 4)

Leak testing
Rubin (1961); Graham (1964); Roehrs (1967); Pilborough (1971, 1989); Blackmar (1973); Bloomer and Smalley (1975); Leslie and Ferguson (1985); Anon. (1987t); Palluzzi (1987)
BS 3636: 1963

Leak monitoring
British Gas (Appendix 27 *Leakage Control*); NRC (Appendix 28 *Leak Detection*); CONCAWE (1973 5/73); D. Harrison and Watkins (1983); Watanabe and Himmelblau (1986); Saiga *et al.* (1991); Stouffs and Giot (1993)

Non-destructive testing
ASTM (STP 112, 145, 213, 1965 STP 371, 1977 STP 624); NRC (Appendix 28 *Nondestructive Examination*); Welding Institute (Appendix 27, 28, 1972/19, 1974/27); McMaster (1959); Hogarth and Blitz (1960); D.M. Lewis (1961); Gleekman (1966); Nittinger (1966); Parrish (1966); Birchon, Bromley and Wingfield (1967); Ostrofsky (1968); Egerton (1969); D.J. Evans (1970); Welding Institute (1972/19, 1973/23, 1974/27); Birchon (1975, 1988); Detlor (1975); Holloway and Kellum (1975); Callister (1976); Erskine (1976b); Gumm and Turner (1976); L. M. Rogers (1976); British Gas (1979 BGC/PS/CP/SND1, 1987 Comm. 1346); Stinchcomb (1980); Buhrow (1983); Laskowski (1984); Nichols (1984); AGA (1986/45); R.K. Miller and McIntyre (1987); Weisweiler and Sergeev (1987); Institute of Materials (1989 B447); Kletz (1989d); Sattler (1989a–d, 1990); Dressel, Heinke and Steinhoff (1991); Sadler and Matusz (1994)
BS (Appendix 27 *Non-Destructive Testing*)

Radiography
ASTM (STP 28A); Wiltshire (1957); L.A. White (1963); Rockley (1964); Halmshaw (1971); Welding Institute (1973/23); Dishart and Bruce (1975); Chynoweth (1986)
BS 2600: 1973–, BS 5288: 1976, BS 5650: 1978, BS 2910: 1986

Dye penetrant methods
BS 6443: 1984

Magnetic particle methods
ASTM (STP 62, 85, 1965 STP 371); British Gas (1992 DAT43)
BS 6072: 1981, BS 4069: 1982

Eddy current methods
NRC (Appendix 28 *Eddy Current Inspection*); G. Johnson and McFarlan (1978); ASTM (1981 STP 722); Holloway, Bauer and Pittman (1981); AGA (1989/64, 1990/70, 1992/87)

Non-destructive identification
Feigel (1958); Imgram and McCandless (1972); ASTM (1973 STP 550); Duff (1976); Ostrofsky (1980–); M.J. Bowen and Campbell (1986); Anon. (1989 LPB 86, p. 23); R.J. Sherwood (1989)

Condition monitoring, performance monitoring
Collacott (1976b, 1977b); de Guerin (1977); Henry (1979); M. Neale and Associates (1979); M.J. Neale (1980); Sims (1980); B. Stephenson (1981); Stewart Hughes (1981); D.W. Butcher (1983); Ghia *et al.* (1983); D. Harrison and Heath (1983); R.M. Stewart (1983); Thomson and Deans (1983); Dodd (1984); Grantom (1985); Meeker (1985); D. Thomas (1985); P. Cooper (1986–); Pocock and Allen (1986); R. Smith (1986); Chesterton Int. (1987); English (1987); J.B. Smith (1987); G. Baker (1989); IMechE (1990/120); AGA (1991/16); Darling (1991); Rao (1991)
BS (Appendix 27 *Condition Monitoring*)

Vibration monitoring
Rathbone (1939); Collacott (1947, 1975, 1976a, 1977a,b); Yates (1949); Blake (1964, 1966); Nittinger (1964); Buscarello (1968); Maten (1967, 1970); C. Jackson (1969, 1972b, 1974, 1975–); Bently (1970); Fieldhouse (1970); R.L. Martin (1970); R.H. Wallace (1970); Beranek (1971); Tustin (1971); D. Wright (1971); Borhaug and Mitchell (1972); P.J. Brown (1972); Erskine (1973, 1976a); Maddox (1973, 1977); Bentley (1974); Black *et al.* (1974); Diehl (1974, 1975); Lorio (1974); Nicholls (1974); Prentice, Smith and Virtue (1974); ASME (1975/34); Harry and Shipp (1975); IMechE (1975/24, 1977/43); R.S. Morrow (1975); O'Dea (1975); Pekrol (1975); Schanzenbach (1975); Beebee (1976); Biggs (1976); Harker (1977); M.H. Price (1977); Irwin and Graf (1979); Broch (1980); Hitchen (1980); J.H. Maxwell (1980, 1981); API (1981 Std 678, 1986 Std 670); Crawley and Erskine (1981); L.L. Fisher (1981); Tan and Dawson (1983); Goldman (1984, 1986); Spencer and Hansen (1985); Barratt (1986); Gorter and Klijn (1986); Leblanc (1986); Goggin (1987); G.R. Kent (1989); Serridge (1990); Scheithe (1992); B. Sheppard (1992); Haq (1993); Heckman (1993); Hussain (1993); ANSI S series, ANSI S2.2–1959, ANSI S2.5–1962, ANSI S2.10–1971, ANSI S2.4–1976; BS 4675: 1976–; VDI 2056: 1964, VDI 2062: 1976
Vibration: Morse (1936–); Collacott (1947); Jacobsen and Ayre (1958); C.T. Morrow (1963); Crede (1965); R.H. Wallace (1970); Cremer and Heckle (1973); Timoshenko, Young and Weaver (1974); Meirovitch (1975); C.M. Harris and Crede (1976); Bishop and Johnson (1979); Lalanne, Berthier and der Hagopian (1983)
ISO 3945: 1985

Loose parts monitoring
NRC (Appendix 28 *Loose Parts Monitoring*)

Balancing and alignment
C. Jackson (1971a,b, 1976a,b); Sandner (1978); Broch (1980); M.G. Murray (1980a); Bloch (1991)
ANSI S2.7–1982; ISO 2371: 1974, ISO 2953: 1985; VDI 2060: 1966

Ultrasonics
ASTM (STP 101, 1986 E100); Filipczynski (1960); Tribolet (1964); Krautkramer and Krautkramer (1969); Newman, Ryden and Lamb (1970); Ostrofsky and Heckler (1970); Welding Institute (1971/15); Marlow (1975); Weatherburn and Clinck (1976); Browne and Constantinis (1983); Fousek (1983); Crocker (1985); Schmer and Goodman (1990); AGA (1991/71)
BS 3923: 1972–, BS 4331: 1972–, BS 4124: 1991

Thermal image monitoring, thermography
Prescott (1972); H.C. Wright (1973); Bichard and Rogers (1976a,b); Norda (1976, 1977); Weismantel and Ramirez (1978); Lister (1980); Imgram and McCandless (1982); B.G. Jones and Duckett (1985); Tuss (1985); Anon. (1986m); Baker-Counsell (1986c); Anon. (1990a); Miljure (1992); B. Smith (1992)

Acoustics, acoustic emission monitoring
NRC (Appendix 28 *Acoustic Emission Monitoring*); Witt (1971a); ASTM (1972 STP 505, 1975 STP 571, 1979 STP 697, 1987 E1211, 1989 E610–89A, E1062, 1991 E569–91E1); ASME (1975/56, 128, 1982, 1983, 1989); Diehl (1975); Koerner, Lord and Deisher (1976); Nichols (1976a); Parry (1976, 1980); Bloch (1977b); Anon. (1979 LPB 27, p. 59); Fowler (1980, 1986, 1987, 1988, 1992); Fowler and Scarpellini (1980); Adam (1982); Cole (1983, 1988, 1990, 1992); L.M. Rogers and Alexander (1983); Treleaven (1983); Wylde and Shaw (1983); International Study Group on Hydrocarbon Oxidation (1985); M.P. Kelly (1985); Pollock (1986); L.M. Rogers (1986); Clough (1987); Heiple and Carpenter (1987); SPI (1987); Frieshel and Jones (1988); Prasek (1988); Zhang (1988); AGA (1989/62, 63); Monsanto Corp. (1990); AAR (1991); Cole and Hunter (1991); Hewerdine (1991, 1993); Vahaviolos, Pollock and Lew (1991); Gandy and Bailey (1992); Bouchard, Payne and Szysko (1994)

Strain measurement
Shannon (1973); L.M. Rogers (1976)

Electrical resistance measurement
Moreland (1976)

Holography
Butters (1971); H.M. Smith (1975)

Wear monitoring, oil analysis, debris examination
Bond (1965); A.E. Davies (1972); Drust (1972); M.G. Murray (1975); D. Scott (1975); Collacott (1976a,b, 1977b); Ricca and Bradshaw (1984); Wilkie (1987a); Rudston (1989)

Radioactive tracers
Brennan (1962); Charlton (1976)

Corrosion monitoring
Ailor (1971); R. Lee (1972); Luddeke (1975); Hancock and Clifton (1976); Rowlands and Moreland (1976); Arnold (1978); Harrell (1978); Hines (1978); Moreland and Hines (1978); Rak (1978); Whitney (1978); Rothwell (1979); Anon. (1981d); Strutt, Robinson and Turner (1981); Biarnes (1982); Sagüe and Davis (1982); Asher *et al.* (1983); Dawson, Eden and Hladky (1983); Diacci, Rizzi and Ronchetti (1983); M.J. Robinson and Strutt (1983); Baker-Counsell (1985b,g); Gregory (1985); M. Turner and King (1986).
External corrosion: Batterham (1985)

Interpretation
Welding Institute (1969, 1972/19); D. Scott and Smith (1975); Bellingham and Lees (1976a,b); Boogaard (1976); IMechE (1976/31); Collacott (1977b)

Risk-based inspection
Ichikawa (1985, 1987); Research Task Force on Risk-Based Inspection Guidelines (1992)

Underwater inspection
Bayliss, Short and Bax (1988)

gasholders and gas cylinders and containers for transport, but not for other pressure vessels. Thus many pressure vessels containing hazardous substances were not subject to specific statutory controls. Moreover, the pressure system components which were the subject of statutory requirements were strictly limited. Principally they were the protective devices associated with steam boilers and receivers and air receivers. Thus many pressure system components containing hazardous substances, including pipework and other components listed in Section 19.3, were not subject to specific statutory requirements. However, although many pressure systems were not covered by specific statutory controls, the general duty to provide safe equipment, which is strengthened by the Health and Safety at Work etc. Act 1974, might be considered to require that the integrity of pressure systems handling hazardous substances should not be less than that of systems handling steam and air.

The Pressure Systems and Transportable Gas Containers Regulations 1989 (the Pressure Systems Regulations), described in outline in Chapter 3, have introduced comprehensive controls on pressure systems as well as pressure vessels. Guidance on these regulations is given in HS(R) 30 *A Guide to the Pressure Systems and Tranportable Gas Containers Regulations* 1989 (HSE, 1990). The regulations are supplemented by COP 37 *Safety of Pressure Systems* (HSE, 1990). The scope and general requirements of the Pressure Systems Regulations are described in Chapter 12 and the those for inspection are described here.

It is normal industrial practice to exercise close control of all parts of a pressure system, including both pressure vessels and other components, and to do this throughout the life of the system, starting with design and continuing through fabrication, installation, commissioning, operation, inspection, maintenance and modification, by means of external and in-house standards and codes. The inspection system is the main means of exercising this control after the design stage.

Nevertheless, in the UK there have in the past been some differences between pressure vessels which were covered by specific regulations and those which are not. In general, with the former the letter of the law applied, whilst with the latter the degree of flexibility based on engineering judgement was rather greater.

One aspect which is of particular importance is the inspection interval. Basic statutory inspection intervals were 14 months for steam boilers and 26 months for large steam boilers, steam receivers and air receivers. In principle, dispensations for longer intervals might be granted by the Health and Safety Executive (HSE), but these were difficult to obtain and it remained the case that the statutory inspection intervals for these items are an inhibiting factor in industry.

As described in Chapter 12, the Pressure Systems Regulations extend the scope of pressure systems to cover essentially all systems which depart significantly from atmospheric pressure. They create a requirement for a formal system of records and examinations. Regulation 5 requires that certain information be provided about the pressure system, Regulation 8 that there be a written scheme of examination, Regulation 9 that examinations be conducted in accordance with this written scheme and Regulation 13 that records be kept.

Regulation 5 requires that sufficient information be provided about the pressure system in respect of design, construction, examination, operation and maintenance, and about any repairs or modifications made to it.

Regulation 8 requires that there be a written scheme for the periodic examination by a competent person of

(a) all protective devices;
(b) every pressure vessel and every pipeline in which (in either case) a defect may give rise to danger; and
(c) those parts of the pipework in which a defect may give rise to danger.

It states that such a scheme shall not be drawn up unless it is suitable and

(a) specifies the nature and frequency of examination;
(b) specifies any measures necessary to prepare the pressure system for safe examination other than those it would be reasonable to expect the user (in the case of an installed system) or owner (in the case of a mobile system) to take without specialist advice; and
(c) where appropriate, provides for an examination to be carried out before the pressure system is used for the first time.

Before the regulations were made, there was much discussion as to how 'pipework' should be covered. The term has been widely defined but the *Guidance* states that the effect of Regulation 8 and of COP 37 is to exclude most 'pipework' from the written scheme.

In contrast to the legislation which they replace, the regulations do not give specifed intervals for any equipment; the intervals formerly specified for steam boilers and for steam and air receivers are not carried forward. In practice, however, these intervals are often retained in examination schemes.

Regulation 9 requires that the examination be performed by a compent person and that a written report be produced of the examination. The report should: state which parts have been examined, the condition of the parts and the results of the examination; specify any repairs or modification required and the date by which they should be done; give the date beyond which the equipment should not be operated without further examination; and state whether the scheme of examination is suitable or whether it needs modification, and if so why.

Regulation 13 requires that records be kept which include: the basic information specified in Regulation 5; the report of the last examination; the previous reports where they contain information on whether the system is safe to operate or whether any repairs or modifications to the system can be carried out safely; and information on any postponement of an inspection beyond the previously specified date.

The statutory controls are not the only external influence which industry has to consider. Adherence to a system similar to the statutory one is generally a condition of obtaining insurance. Much inspection of process plant is in fact carried out by insurers.

19.2.2 Inspection bodies

There are a number of parties who may conduct inspection of a pressure vessel during its manufacture. They include (1) government, (2) the manufacturer, (3) the user, (4) an insurer, and (5) a consultant. The same set of parties, except for the manufacturer, may undertake inspection during operation.

Government inspection may be undertaken for two rather different purposes. One is to assure the quality of the government's own purchases, and the other is for regulatory purposes.

In the UK, the requirements of government, particularly in defence, have greatly influenced the evolution of inspection systems. Mention should be made in particular of the Aeronautical Inspection Directorate (AID), renamed in 1969 the Aeronautical Quality Assurance Directorate (AQD), which has developed an inspection system which is the basis of many contracts by government and by other organizations. Some basic principles of the system are that: there must be verification that every requirement of every specification and drawing has been met; there is a complete chain of responsibility for inspection at every stage; and there are full inspection records. The manufacturer's inspection system has to be approved. His subcontractors also have to be approved or else special arrangements made. The full requirements of the system are expensive, however, so that a user who does not require this degree of control may adopt a modified system.

It will be apparent that this system was a forerunner of the quality assurance systems, based on BS 5750 and ISO 9000, which are now becoming widespread throughout industry.

A different type of government involvement is inspection by government inspectors in relation to statutory requirements under such legislation as the Factories Act 1961 or the Nuclear Installations Act 1959.

The manufacturer usually has his own inspection system to assure quality. In some cases the user may be involved in specifying the type of inspection system which the manufacturer should operate. Often the user sends his inspectors to carry out inspections of the equipment during its manufacture. This is routine procedure with large oil and chemical companies.

Pressure vessels are often built to the survey of insurers, particularly in the oil and chemical industries. The oldest and best known insurance organization is Lloyds of London and the certification 100 A1 at Lloyds is an accepted cachet of high quality.

Inspection is also carried out by consultant engineers, some of whom specialize in this work.

19.2.3 Approval organizations

In the UK, the *Report of the Committee of Enquiry on Pressure Vessels* (Ministry of Technology, 1969a) led to the setting up of the Pressure Vessel Quality Assurance

Board (PVQAB) in 1981. The PVQAB operates a system of approval for inspection organizations.

In the USA, an approval system is operated by the National Board of Boiler and Pressure Vessel Inspectors (the National Board).

19.2.4 Inspection organization

Within the company, it is essential to have a management system which ensures effective control of all aspects of the plant, and in particular of the pressure system, throughout all the stages of its life. Such a management system was described in Chapter 6.

The inspection organization plays a key role in this system. It is responsible for the intial inspection of new equipment during its fabrication and construction, and for the periodic inspection of operating equipment throughout its working life.

The framework within which the inspection organization operates is determined by the design and operating authorities. The design authority should determine the parameters within which the plant is to operate, should specifiy the design codes and should carry out the actual design. It should also specify the standards for fabrication, construction and testing and should prescribe the documentation required on these aspects. The operating authority should provide a code for the regular inspection of the plant. In addition, it should create a system to control both plant and process modifications.

The inspection organization may be a part of the design authority or it may be an external body such as an engineering inspection agency or an insurance company, but whatever arrangement is adopted the inspection organization should be independent of the operating authority.

In many cases the inspection work is divided between the company's own inspection organization and an external inspection agency. In particular, outside inspectors are commonly used to carry out the statutory inspections of steam boilers and receivers and air receivers.

The inspection organization is concerned normally with pressure vessels, pipework and protective devices. The inspection of many other types of equipment such as rotating machinery or instrumentation is carried out by the appropriate specialists, who are usually not part of the inspection organization.

19.2.5 Competent persons

Inspection is a specialist matter and should be done only by a qualified inspector. For statutory equipment such as steam boilers the competence of the inspector has been a specific requirement of the Factories Act 1961, Section 33(9).

The question of the competent person for the inspection of boilers and pressure vessels was considered in the *Report of the Advisory Committee on the Examination of Steam Boilers in Industry* (Honeyman, 1960) (the *Honeyman Report*). The report states in connection with the requirement for a competent person:

> What appears to be contemplated is that the person should have such practical and theoretical knowledge and actual experience of the type of machinery or plant which he has to examine as will enable him to detect defects or weaknesses which it is the purpose of the examination to discover and to assess their importance in relation to the strength and functions of the particular machinery or plant.

The Pressure Systems Regulations 1989 require that certain functions such as approval of the scheme of examination for pressure vessels be done by a competent person. This is discussed further in Section 19.3.

19.2.6 Inspection in manufacture and operation

Inspection activities cover the stages of (1) manufacture, (2) commissioning, and (3) operation. It is hardly necessary to emphasize that the existence of an inspection system and the presence of an inspector has an important influence on the quality of the work done. Frequently the function of inspection is combined with that of progressing the work, since this has been found to be an effective way of reducing lead times.

An important aspect of inspection is planning. Specifications and drawings should be made available to the inspector as early as possible so that he can plan the stages of inspection. The inspector should try to make sure that the manufacturer's personnel are fully informed of the inspections required at the different stages of fabrication. The inspection of features such as the base metal properties and the dimensions of components should be timed to fit in with the overall fabrication schedule.

The results of inspections should be recorded as detailed inspection/test reports, but in addition it is normal to issue release notes or inspection statements, which are less detailed, or, in the case of non-acceptance, a rejection note.

The inspection of welds and other features is discussed below.

Inspection of pressure vessels during commissioning covers essentially similar features together with pressure and leak tests and other commissioning tests as described in Sections 19.7 and 19.8.

Inspection of pressure vessels during operations is carried out regularly according to a system such as that defined in Section 19.3. This relies basically on visual examination supplemented by other methods of non-destructive examination and non-destructive testing and by condition monitoring methods. In some cases pressure testing is necessary.

The basic principles of inspection apply also to the inspection of other equipment such as rotating machinery. In this case, however, the inspection is particularly concerned with checking the condition of the main components of the machine, the performance of the machine under the various test conditions specified and the alignment and balancing of the installed machine, as well as the condition and performance of ancillary equipment such as lubrication systems.

A certain amount of information is available in the human factors literature on errors in inspection. The main finding is that the probability of detecting a defect decreases as the probability of the defect decreases.

19.2.7 Inspection of welds

One of the most important aspects of the inspection of pressure vessels is checking the quality of welds. The methods of welding were described in Chapter 12. Minimum inspection requirements for the fabrication of

welds are laid down in BS 5500: 1991 and other standards. Welds are also one of the main aspects inspected in regular inspections during operation.

An inspection system exercises control of weld quality by (1) approval of welders, (2) specification of welding materials, (3) specification of welding methods, and (4) examination/testing of welds.

There are standard qualifications and tests for various classes of welder, including BS 1295: 1987, BS 4872: 1976– and the ASME *Boiler and Pressure Vessel Code, Section IX*. In general, a welding method is specified, giving details of electrodes, welding rods, flux, shielding, metal preparation, actual welding, heat treatment and testing.

Visual examination of a weld should ensure (Pilborough, 1971):

(1) freedom from undercut, cracks, craters, blowholes and marked irregularities;
(2) correct profile;
(3) good appearance – a smooth even finish and freedom from pockets will avoid the possibility of stress concentrations leading to cracking;
(4) smooth joins where new electrodes have been started;
(5) good penetration at the root of the weld, as judged from the bead on the underside (in the case of a butt weld) prior to the application of the sealing run.

Illustrations of typical weld defects are given in BS 499: 1980 – *Welding Terms and Symbols*.

In some cases pressure vessels are fabricated on site, because they are too large to be transported. The conditions of site fabrication often make it advisable to carry out more comprehensive checks on materials and welds than the minimum code requirements.

19.2.8 Inspection of other features

Other features which are examined in pressure vessel inspection include:

(1) equipment dimensions;
(2) base metal;
(3) surface condition;
(4) wear situations;
(5) high stress situations;
(6) dissimilar metals;
(7) stray electric currents;
(8) gaskets, seals and joints;
(9) lagging;
(10) protective finishes;
(11) venting and draining;
(12) access.

The inspection should check that the dimensions of the equipment are within the permitted tolerances, that the base metal used is that specified, and that it has met the requirements. The condition of the metal surface should be inspected for defects which may give rise to crack growth. A check should be made on assemblies which may be subject to wear and on stress raisers such as sharp angles, changes of section and attachments such as nozzles or lugs. The presence of dissimilar metals and stray electric currents which may give rise to corrosion should be considered. The suitability of joints, gaskets and seals should be checked, as should that of the lagging and protective finishes. The adequacies of the vents and drains on the vessel should be confirmed and the means of access reviewed.

Other aspects of inspection, such as tests during commissioning and pressure and leak testing, are considered in Sections 19.1, 19.7 and 19.8, respectively.

19.2.9 Inspection register and records

It is essential to keep a register of the equipment to be inspected and records of the results of the inspections. The precise contents of the register depend on the item concerned, but in general should include:

(1) identification number, order number and drawing number;
(2) specification, design parameters, process fluids;
(3) inspection/test reports during manufacture;
(4) inspection category, interval, method;
(5) special features relevant to deterioration, failures;
(6) materials/parts list;
(7) design life/remanent life prediction;
(8) date of entry into service.

Such a register is equally appropriate to pressure vessels, protective devices, rotating machinery or instrumentation.

The specific information requirements given in the IP *Pressure Vessel Examination Code* for the registration of pressure vessels are described in Section 19.3.

For a pressure vessel there should be full information on the inspections/tests done during its manufacture, including reports on tests on the material of construction, radiographs or other records of tests on welds, and reports on pressure and leak tests.

Reports of the regular inspections/tests on the equipment should be prepared and filed in the register. These reports should generally cover the results of the main inspection/test and of any additional monitoring and tests, any deterioration or failure detected and repairs carried out, and any modifications or changes of duty.

9.3 Pressure Vessel Inspection

The inspection of pressure vessels and their protective devices is crucial to the maintenance of the integrity of the pressure system and is a principal activity of the inspection authority.

Pressure vessels come within the Pressure Systems Regulations 1989 and are covered in the guidance HS(R) 30 and in COP 37. A relevant code is the *Pressure Vessel Examination Code* by the Institute of Petroleum (IP) (1993 MCSP Pt 12). The account of pressure vessel inspection given here is based primarily on this code.

19.3.1 Competent person

The IP *Pressure Vessel Examination Code* defines the competent person as the person or body authorized by the user to draw up or approve the scheme of examination and to perform the examination. In the UK, the competent person may be company personnel or an external body specializing in the inspection of pressure vessels. The attributes of the competent person are given in COP 37.

19.3.2 Design authority

The design of the pressure vessel is the responsibility of the design authority. The IP *Pressure Vessel Examination*

Code states that the design authority may be a vessel design group responsible to the user, an authorized design contractor, an independent design consultant, the engineering authority or the competent person. In some countries the design authority is a state agency.

19.3.3 Engineering authority

The engineering authority is responsible for the maintenance of the pressure vessel and is authorized to do this by the user.

19.3.4 Definition

In considering an inspection scheme, it is necessary first to define the equipment which is to be brought within the scope of the pressure vessel inspection system. The IP *Pressure Vessel Examination Code* defines a pressure vessel as follows:

> A closed vessel consisting of one or more independent chambers, any or each of which may be subject to an internal pressure greater than 0.5 barg, or as defined by National Legislation.

The code explicitly excludes vessels subject to pressure solely by static head and storage tanks designed and constructed to codes and standards such as BS 2654 and BS 2594.

This definition of a pressure vessel supersedes that given in the previous *Pressure Vessel Inspection Safety Code* by the IP (1976 MCSPPt 12) which was:

> (i) A closed vessel of not less than 0.1 m^3 capacity consisting of one or more independent chambers any or each of which may be subject to an internal pressure greater than 70 mbar gauge or less than 930 mbar absolute or
> (ii) A closed vessel wherein $P \times V > 1$ where P is the internal pressure in bars and V is the enclosed volume in cubic metres.

Also of interest is the definition given in the ICI *Pressure Vessel Inspection Code* for vessels falling within the scope of that code:

> A pressure vessel is a closed vessel of any capacity consisting of one or more independent chambers, any or each of which is or may be subjected to internal pressure greater or less than atmospheric.

This definition includes:

> (a) Vessels not normally subject to internal pressure but in which internal pressure would occur in the event of a failure of any part, maloperation, isolation or other circumstances, for example, the failure of an internal steam coil in a vessel not adequately vented to prevent a pressure rise.
> (b) Vessels in which vacuum can develop, for example, steam receivers, steam condensers and other vessels containing condensable gases and vapours.

For other equipment the code states:

> Consideration should also be given to the registration and routine inspection of other items which although not normally classified as pressure vessels may give rise to hazardous situations, e.g. fired equipment, large diameter piping, expansion bellows, and pressurized equipment subjected to erosive or corrosive conditions. Where cross-country pipelines are employed special arrangements will be necessary for their routine examination.

The IP *Pressure Vessel Examination Code* defines a protective device as:

> A device designed to protect the pressure system against system failure and certain devices designed to give warning that system failure might occur, safety valves, bursting discs or combination of both.

The definition of a protective device given in the ICI *Pressure Vessel Inspection Code* is:

> Any automatic device which protects equipment from over-pressure, over-temperature, over-filling, corrosion, explosion or other hazardous conditions; including atmospheric vents, lutes, flame traps, deadweight flaps, some non-return valves, relief valves, fusible plugs, bursting discs and instrumental trip systems, many of which incorporate an advance alarm indication.

The ICI *Code* also lists equipment which, subject to approval, may be excluded from the requirements of the code itself, although it may still require some degree of inspection. Some important items in this list are vessels subject to static head only or to applied pressure not exceeding +0.07 bar (+1 $lb_f/in.^2$) and not subject to corrosive risks; parts of prime movers and machines driven by them; protective devices whose failure does not result in a hazard.

19.3.5 Registration

A pressure vessel identified as such should be registered before it is brought into service. The system given by the IP *Pressure Vessel Examination Code* is broadly as follows.

The vessel should be given an identification number and there should be created for it a records file and, where applicable, a scheme of examination.

The required contents of a records file as described in the IP *Code* are essentially similar to those given in the ICI *Pressure Vessel Inspection Code*, which are as follows:

> For equipment the file shall include its identification number, the order number, the drawing reference, specifications, materials lists, inspection reports during manufacture, test certificates relating to the material and tests on the completed equipment. It shall also contain details of the design conditions, the process fluids, of the expected operating conditions, and the date of entry into service. In addition, the file shall include a note of any special kinds of deterioration – e.g. stress corrosion – to which the equipment may be subject.

The IP *Code* requires that the information include the safe operating limits of the vessel and, where available, the limit criteria for its retirement with notes on their derivation.

The record file should give the equipment classification and inspection categories. It should specify the initial and subsequent inspection intervals, the type of inspection to be done and, where appropriate, the inspection acceptance standards.

To this initial information should be added other relevant information generated during the life of the equipment. This includes: reports of periodic inspections and tests; reports of failures, failure examinations and

repairs; records of corrosion and other condition monitoring; and details of modifications or changes of duty. Where a document cannot be kept in the record file itself, there should be a cross-reference to it.

The registration of protective devices is along broadly similar lines. The IP *Code* requires that its record file contain information on its function and operation, including drawings, a specification of the duty, supplier's details on the style and type of device, materials of construction and any special features, together with reports of examinations and tests.

19.3.6 Classification

A pressure vessel is generally classified according to whether or not it is subject to legal requirements for inspection. The IP *Pressure Vessel Examination Code* assigns a vessel to Classification A or B. Class A includes all vessels and their protective devices which are subject to periodic examination in accordance with national or regional legal requirements. The extent of the classification is therefore a function of the country or state where the vessel is to be used. Class B includes all vessels and their protective devices not assigned to Class A. It covers all vessels which are not subject to legal requirements.

Where the legal requirements permit, Class A pressure vessels and protective devices should be further allocated to a grade, namely to Grade 0, 1, 2 or 3, as described in Section 19.3.7.

The code states that the regulatory requirements in the UK are primarily aimed at ensuring the periodic examination of equipment which contains significant quantities of stored energy from compressible fluids and that many items of equipment which contain flammable or toxic liquids are effectively exempt, but that such examination is nevertheless beneficial, and it suggests that the inspection philosophy described for Class A equipment be applied to Class B equipment also.

19.3.7 Grading

As stated above, the IP *Pressure Vessel Examination Code* requires that, where legal requirements permit, the pressure vessel and its protective device be allocated to a grade. The grade indicates the maximum interval which may elapse between major examinations.

The principles of grading are that: the vessel receives a pre-commissioning examination before entering service; it is initially allocated to Grade 0 and is given a first thorough examination after a relatively short period of service; it is then either retained in Grade 0 or allocated to Grade 1 or 2; subsequently, after a second thorough examination, it is allocated to Grade 1, 2 or 3; and, as it approaches the end of its design life or predicted remanent life, it is reallocated to a lower grade if necessary.

Equipment is allocated to Grade 0 when it first enters service and also where the foreseeable deterioration is at a fairly rapid rate, but still consistent with this grade, or where there is insufficient knowledge of operational effects to predict its behaviour in service.

Equipment is allocated to Grades 1 or 2 where deterioration is at a rate which is predictable and consistent with the grade, the knowledge of its actual behaviour justifies allocation to the grade, or where there are reliable means of assessing the operational effects and/or the associated deterioration.

Equipment is allocated to Grade 3 where deterioration is at a rate which is low and consistent with the grade, or the knowledge of actual service conditions justifies allocation to the grade.

Transfer between grades, either upwards or downwards, is made on the basis of the examinations.

A variation to this procedure may be used where a group of vessels are substantially the same with regard to design and construction and to conditions of service so that they may reasonably be expected to deteriorate in a similar way and, where the appropriate grade is Grade 1 or above, grading may be based on sample examinations of vessels in the group. The IP *Code* gives the rules governing this procedure.

Another permitted variation applies where a substantially new vessel is the same with regard to design and construction as an existing vessel and is to be used under the same, known conditions of service. In this case the vessel may be allocated the same grade as the existing vessel.

A grading review of a vessel is required in any one of the following circumstances: (1) there is a significant change in its conditions of service; (2) an abnormal incident has occurred which could affect its deterioration; (3) on-line inspection indicates a significant change in its condition; or (4) it is approaching its design life, or it is proposed to extend its service life beyond the design value.

The grading of protective devices is subject to two general principles. The interval between examinations for the device should not exceed that for the vessel protected and it should not exceed that given in Section 19.3.8. Factors which govern the inspection interval are discussed in Chapter 13.

19.3.8 Examination intervals

The maximum examination intervals given in the IP *Pressure Vessel Examination Code* are shown in Table 19.10, Section A. The longest of these maximum intervals is therefore 144 months, or 12 years. On the basis of the classification of equipment it is possible to specify inspection categories which define the interval between inspections.

19.3.9 Examination principles

The IP *Pressure Vessel Examination Code* states that the purpose of examination is:

> To ensure that equipment remains in a satisfactory condition for continued operation consistent with the prime requirements of safety, compliance with statutory regulations and economic operation until the next examination.

The code distinguishes between the pre-commissioning examination, the first examination (after the vessel has been put into service) and subsequent examinations. The purpose of the pre-commissioning examination is to ensure that the examination and tests specified for the manufacture of the equipment have been done, that the documentation is in place with a record of any significant defects, that there is a basis for the assessment of deterioration in future examinations and that a check is made to ensure that no damage has occurred since the examination during manufacture. The first in-service

Table 19.10 *Maximum examination intervals for pressure vessels, protective devices and piping systems (Institute of Petroleum, 1993 MCSP Pts 12 and 13) (Reproduced by permission)*

A Pressure vessels and protective devices				
Equipment	*Recommended maximum examination period (months)*			
	Grade 0	*Grade 1*	*Grade 2*	*Grade 3*
Process pressure vessels and heat exchangers	36	48	84	144
Pressure storage vessels	60	72	108	144
Protective devices	24	36	72	–
B Piping systems				
Equipment	*Recommended maximum examination period (months)*			
	Grade 0	*Grade 1*	*Grade 2*	*Grade 3*
Piping systems	36	48	84	144

examination is done to ensure that any defect in design or materials is detected and that suitable components are selected, examined and measured, so as to form the basis for the assessment of corrosion or wastage in future examinations.

The ICI *Pressure Vessel Inspection Code* defines the objectives of inspection as follows:

> The objective of vessel inspection is to detect any deterioration such as corrosion, cracking or distortion indicating possible weaknesses that may affect the continued safe operation of the vessel. Primarily inspection should be visual, but it shall be supplemented by other techniques and measurement when necessary to determine the extent of any losses of thickness, pitting, cracking, etc. Resorting to a pressure test as the sole method of periodic inspection is an inferior alternative to examination and should be used only when examination is not practicable or the findings of the visual examination are inconclusive.

The inspection should also include an examination of protective devices.

19.3.10 Examination practices: pressure vessels

The maximum interval between examinations is set by the grade to which the vessel is allocated. The IP *Pressure Vessel Examination Code* gives a number of addtional factors which are to be taken into account in deciding on the actual interval. These include: any regulatory requirements; the works policy; the severity of the duty; the performance of other vessels on similar duty; the ability to carry out meaningful on-stream inspection; and the remaining design life and the predicted remanent life. Other factors in particular applications are catalyst life and regeneration intervals, and performance of internal linings. It is also necessary to consider the consequences of failure.

The IP *Code* also refers by way of caution to three aspects that may require special attention: (1) lined vessels; (2) internal fittings; and (3) external lagging, cladding and fireproofing. Lining failure may cause a vessel to deteriorate rapidly and this should be taken into account in setting the examination interval. Internal fittings hinder inspection and are often difficult to remove, but may also promote deterioration; they should be removed as necessary to permit adequate examination. Parts of the outer shell and features such as anchor bolts, skirt attachments and saddle support surfaces may need to be checked at each examination. Sections of lagging or fireproofing may need to be removed for examination where conditions favourable to external corrosion exist.

There are various preparatory measures which need to be taken before an inspection is carried out. The inspector should brief himself on the history of the vessel and, where applicable, on that of other similar vessels.

The vessel is normally taken out of service, isolated, emptied and cleaned. The surfaces of the vessel are then exposed and prepared for examination. This may involve such measures as cleaning of internal surfaces, the removal of some internal fittings and the removal of lagging from the outside of the vessel. These activities should be covered by appropriate procedures and permit-to-work systems, as described in Chapter 21. The examination is then carried out.

The matters to be recorded following the examination are given in the IP *Code*. They should cover: the scope of the examination; the items examined and the examination techniques used; a qualitative description of the findings backed up by a quantitative measure; a specification of any repairs or modifications required; relevant repair and non-destructive examination procedures; a note of any changes to the safe operating limits or any remanent life predictions; a review of the scheme of examination and the grading previously selected; and a date for the next examination. The *Code* gives an appendix containing examples of examination reports.

The IP *Code* recognizes the value of on-stream methods of examination, but states that in general they complement rather than replace visual examination.

19.3.11 Examination practices: protective devices

The IP *Pressure Vessel Examination Code* divides protective systems into pressure-actuated devices and other devices. In the former category it discusses regular

safety valves, pilot-operated safety valves and bursting discs.

For a safety valve the code requires that the valve be removed, immediately tested on a suitable test rig to determine the pressure at which the valve would have lifted in service and the results recorded. The valve should then be dismantled, cleaned, repaired, restored, lapped and reset to the correct cold differential test pressure. For pilot-operated safety valves, where it is not normally practical to remove the main valve, the testing is confined to the pilot valve.

In the second category the IP *Code* deals with: fusible plugs; thermal sensors, alarms and trips; sensors and alarms on other variables; and non-return valves.

The *Code* also discusses the need to maintain adequate overpressure protection of the vessel at all times and the isolation practices necessary to achieve this.

19.3.12 Modification and repair

The IP *Pressure Vessel Examination Code* requires that any modification necessary on a pressure vessel should be approved by the design authority and the competent person, and that the design and execution of any modification or repair be under the control of the latter. The effect on any protective devices on the piping system of any modifications or repairs on that system should be considered.

Records should be kept of any modifications or repairs carried out, and should include the original approval procedure documents together with details of materials and techniques, drawings, and test certificates.

Where a vessel has been subject in its construction to stress relief or heat treatment, welding should not be undertaken without the approval of the competent person.

19.3.13 Vessel testing

The IP *Pressure Vessel Examination Code* discusses five forms of testing: (1) strength testing, (2) leak testing, (3) non-destructive testing, (4) destructive testing, and (5) materials analysis. Any of these may be used at the various stages of the vessel's life, but the last two are used mainly at the construction stage or in connection with modification or repair.

Pressure and leak testing are considered in Sections 19.7 and 19.8, respectively.

19.3.14 Defects and failures

An account of defects and failures in pressure vessels is given by Pilborough (1989). Some of the features which may be revealed by an inspection are:

(1) internal corrosion;
(2) surface defects;
(3) weld defects;
(4) wear defects;
(5) deposits and debris;
(6) high stress situations;
(7) inadequate drainage;
(8) external corrosion.

Some of the types of internal corrosion which occur in process plant were described in Chapter 12. Corrosion may reduce not only the thickness of the metal but also its strength. Methods of detection include visual examination, thickness measurement, including measurements by ultrasound, and corrosion monitoring. Changes to a base metal such as graphitization or hydrogen embrittlement may be detected by metallurgical examination.

Surface defects such as cracks or pitting arising from such causes as corrosion, erosion or crack growth may be detected by visual examination or by methods such as magnetic particle or dye penetrant techniques. The avoidance of surface defects is particularly important where there is a risk of fatigue failure, since a rough surface can greatly reduce the fatigue strength of a steel.

These methods of crack detection may also be used to find weld defects. The latter include weld deterioration, which may arise due to the roughness of the weld, or weld decay, which is intergranular corrosion and occurs in austenitic stainless steels.

Cracks may be particularly serious as they can grow and lead to failure. It is often possible to remove a crack from a weld by chipping it out and depositing fresh weld metal. Small cracks may sometimes be stopped by drilling small holes at the extremity, which reduces the stress concentrations.

Wear on moving parts is normally found by visual examination and may result in failure if not rectified.

The build-up of deposits of materials and/or debris can create a hazard if equipment such as pipes and valves, or devices such as vents, pressure relief valves or instruments become blocked. Such deposits are revealed by visual examination.

There are certain undesirable features which, insofar as is practicable, are eliminated in the original design of equipment, but which may be reintroduced by plant modifications. High stress situations may have been created at vessel connections or at lugs. There may be elements which are under stress due to the limitation of thermal expansion or contraction. Similarly, modifications may have been made which impede complete drainage. Visual examination may detect these facts.

External corrosion of the plant is detected by visual examination. It can be severe and can lead to serious loss of metal thickness.

19.4 Pressure Piping Systems Inspection

Most releases occur not from pressure vessels but from the associated piping systems. Inspection of piping systems is therefore important. Pressure piping systems come within the Pressure Systems Regulations 1989 and are covered in the guidance HS(R) 30 and in COP 37. A relevant code is *Pressure Piping Systems Examination Code* (IP, 1993 MCSP Pt 13). The account of pressure piping systems inspection given here is based primarily on this code. The provisions of this code largely mirror those of the *Pressure Vessel Examination Code* (IP, 1993 MCSP Pt 12), and to the extent that this is so they are not repeated here.

The definitions of the competent person, the design authority and the engineering authority for piping systems are essentially the same as those for pressure vessels, with the former term being substituted for the latter one.

19.4.1 Selection

The process of selecting pipework for registration in the inspection system is the equivalent to the definition of pressure vessels. The IP *Pressure Piping Systems Examination Code* states that pipework need not be physically identifed on site by an identification number provided the major plant items are so marked that pressure piping attached to them can be identified.

The criteria for selecting piping for registration are that there is a legal requirement or that the piping is known or suspected to deteriorate and its failure would give rise to an unacceptable situation.

19.4.2 Registration

For new piping the IP *Pressure Piping Systems Examination Code* recommends that the records file contain the identification number, the drawing references, the isometric drawing, specifications, materials lists, the material specification, the constructional acceptance and test certificates, the design data/safe operating limits, the scheme of examination and the retirement limit criteria.

For existing piping the *Code* states that where some of the above information is not available, the recommended records are the identification number, the drawing references, an up-to-date drawing/sketch defining the extent of the system, the piping specification to which repairs or modifications should conform, the design data/safe operating limits, the scheme of examination and a recent assessment report.

For piping sytems there is no process corresponding to that of the classification of pressure vessels, but it is necessary to make arrangements to ensure that unregistered piping systems are neverthelsess examined so that they remain fit for continued service.

19.4.3 Grading

The IP *Pressure Piping Systems Examination Code* states that, where legal requirements permit, a registered piping system should be allocated to a grade.

The principles of grading are that: the piping system receives a pre-commissioning examination before entering service; it is allocated to Grade 0 unless knowledge of service conditions is such that it can be allocated to Grade 1 or 2; subsequently, following the first and second thorough inspections and on the basis of knowledge of service conditions and of the condition of the piping system, it is allocated to Grade 1, 2 or 3; and as it approaches the end of its design life or predicted remanent life it is reallocated, where necessary, to a lower grade.

The detailed rules for grade allocation and grading review of piping systems given in the *Code* are essentially similar to those for pressure vessels. For protective devices the code refers to the IP *Pressure Vessel Examination Code*.

19.4.4 Examination intervals

The maximum examination intervals prescribed by the IP *Pressure Piping Systems Examination Code* are given in Table 19.10, Section B. The longest of these intervals is thus 144 months, or 12 years.

19.4.5 Examination principles

The purpose of the examination of piping systems given by the IP *Pressure Piping Systems Examination Code* is essentially the same as for pressure vessels.

The *Code* distinguishes between the pre-commissioning examination, the first examination (after the piping system has been put into service) and subsequent examinations. For the former it also draws a distinction between new and existing installations. For new installations the purpose of the pre-commissioning examination is to ensure that the examination and tests specified have been done and that the documentation is in place, whilst for an existing installation it is to establish any history of deterioration and to ensure that the condition of the pipework is surveyed. The first in-service examination is done to ensure that any defect in design, fabrication or materials is detected and that suitable components are selected, examined and measured, and the results recorded, so as to form the basis for the assessment of corrosion or wastage in future examinations.

19.4.6 Examination practices

The maximum interval between examinations is set by the grade to which the piping system is allocated. The IP *Pressure Piping Systems Examination Code* gives in Appendix A a number of additional factors which are to be taken into account in deciding on the actual interval. They include: any regulatory requirements; the age and general condition; the severity of the duty, in terms of corrosion, erosion and vibration; the proximity to systems containing corrosive fluids; any abnormal flows; any vulnerable components such as bellows and expansion joints and small bore connections; the pipework supports; any special features; and the ability to carry out meaningful on-stream inspection. It is also necessary to consider the consequences of failure.

Any necessary preparatory measures should be taken before an examination is carried out. These may include the provision of a means of access and lighting and preparation of surfaces.

The matters to be recorded following the examination are given in the IP *Code*. They should cover: the scope of the examination; the items examined and the examination techniques used; a qualitative description of the findings, backed up by a quantitative measure; a specification of any repairs, renewals or modifications required; the relevant repair and NDE procedures; any changes to the safe operating limits or any remanent life predictions; a review of the scheme of examination and of the grading previously selected; and a date for the next examination.

The IP *Code* also refers by way of caution to several aspects that may require special attention: (1) lined pipes; (2) external lagging and fireproofing; (3) valves and fittings; (4) buried piping; and (5) bellows. The considerations relevant to lined pipe and external lagging and fireproofing are broadly similar to those pertaining to pressure vessels. Valves and fittings need special consideration on account of possible casting defects, regions of high turbulence, local stress concentrations due to thermal expansion and other stresses, and vibration. Buried pipelines are usually protected from external corrosion by cathodic protection, but there are vulnerable areas near ground level where protection can break down and corrosion occur. The cathodic protection

(CP) systems themselves should be subject to periodic examination and a record kept of the CP potentials. Consideration should be given to the inspection of the inside of the pipeline by an 'intelligent pig'. Bellows should be examined immediately after commissioning to check: that the relative movement is being absorbed as intended and examined periodically to look for cracks or leaks; for any distortion or yielding of anchors or seizing or binding of guides; for any unanticipated movement of the parent piping; and for any permanent distortion of the bellows.

If the pipework has been subjected to any abnormal operating conditions or other abnormal conditions such as fire, appropriate checks should be made. Possible causes of deterioration may be: damage to bellows; cracking of ferritic alloy or austenitic stainless steels; hardening of air-hardening ferritic alloy steel; or zinc embrittlement of stainless steel.

The examination practices for protective devices are essentially as given in the IP *Pressure Vessel Examination Code*.

19.4.7 On-stream examination methods

The IP *Pressure Piping Systems Examination Code* states that some piping systems may be satisfactorily examined by means of on-stream methods and gives in Appendix B guidance on methods which may be applied.

The methods described are: (A) walking the main; (B) selective and (C) extensive non-destructive testing (NDT) for thickness gauging; (D) selective and (E) extensive removal of insulation and external examination; (F) monitoring by indirect measurement; (G) use of thermal indicators and thermal imaging; (H) profile radiography; and (I) flash radiography. The methods of indirect measurement cited include corrosion probes and coupons and pH recording. The thermal indicators mentioned are temperature sensitive paints or crayons. Profile radiography involves firing a beam tangential to the wall of the pipe and produces a profile image of the internal and external profile of the pipe. Flash radiography is similar but gives information on the external surface.

Features to be checked in walking the main include: damage to the pipe; damage to insulation; the condition of joints, valves and fittings; lack of adequate support; lack of ground clearance; vibration or excessive movement; leaks from or onto the pipe; and abuse of the pipe.

The *Code* also gives in the same appendix the following off-stream methods: (J) hammer testing; (K) pressure testing; (L) internal examination; (M) interval viewing; and (N) special techniques.

19.4.8 Modification and repair

The IP *Pressure Piping Systems Examination Code* requires that any modification made to a registered pressure system should be approved by the design authority and any repair be subject to the approval of the competent person.

The effect on any protective devices on the piping system of any modifications or repairs on that system should be considered. Following modification or repair a grading review should be carried out.

Records should be kept of any modifications or repairs carried out, and should include the original approval procedure documents together with details of materials and techniques, drawings and test certificates.

Where there may have been in the original construction of piping system a requirement for heat treatment, a check should be made and, if it was required, reference should be made to the engineering authority or competent person who should then define any requirements.

19.4.9 Piping system testing

The account of testing given in the IP *Pressure Piping Systems Examination Code* follows essentially that given in the IP *Pressure Vessels Examination Code*, and deals mainly with strength testing by hydraulic or pneumatic pressure tests and with leak testing.

19.5 Non-Destructive Testing

Non-destructive testing techniques are used to detect defects in equipment such as pressure vessels and pipework during both its construction and its operational life.

Equipment is tested by non-destructive testing methods during fabrication. Pressure vessel codes such as BS 5500: 1991 lay down detailed non-destructive testing requirements. These are minimum requirements. For some pressure equipment it may be necessary to carry out more extensive testing. This is particularly the case where equipment has been fabricated on site.

It may be necessary to carry out further non-destructive testing of some equipments during construction and commissioning.

The condition of the equipment during the operation of the plant is checked by non-destructive testing, particularly, but not exclusively, during plant shut-down.

Once the plant is operational, it becomes difficult to obtain access for visual examination of some parts of the equipment, e.g. the internal surface of a refrigerated storage tank, so that non-destructive testing techniques which can be used externally become very attractive.

Accounts of non-destructive testing are given in *Non-Destructive Testing* (Hinsley, 1959), *Techniques of Non-Destructive Testing* (Hogarth and Blitz, 1960), *Principles and Practice of Non-Destructive Testing* (Lamble, 1962), *Non-Destructive Testing* (Birchon, 1975), *Pressure Vessel Systems* (Kohan, 1987), *Non-Destructive Testing of Large Diameter Pipe for Oil and Gas Transmission Lines* (Weisweiler and Sergeev, 1987) and *Inspection of Industrial Plant* (Pilborough, 1989).

Some non-destructive testing and monitoring methods are:

(1) visual inspection –
  (a) boroscopes;
(2) radiography –
  (a) X-rays,
  (b) γ-rays;
(3) ultrasound;
(4) magnetic methods –
  (a) magnetic particles,
  (b) magnetic prints,
  (c) eddy currents;
(5) dye penetrant methods;
(6) stress wave emission monitoring;
(7) holography;
(8) electrical measurements –
  (a) resistivity,

(b) capacitance.

These methods are now described in more detail.

19.5.1 Visual examination

Visual examination is the original and most widely used method of inspection and is non-destructive. Accounts are given in *Visual Examination* (Keymed Industrial, 1983) and by Elonka (1975), Kohan (1987) and Pilborough (1989).

Visual inspection is effective in detecting surface defects ranging from cracks to corroded areas, and defective assemblies.

The range of visual examination can be extended by the use of aids such as periscopes or boroscopes. Boroscopes are available with lens or fibre optics. They are used to examine the condition of internal components such as the blades of turbines and compressors.

BS 5500 requires only visual examination for Category 3 pressure vessels.

19.5.2 Radiography

An important non-destructive testing method is X-ray radiography. Radiographic examination is covered by BS 2600: 1973– *General Recommendations for the Radiographic Examination of Fusion Welded Butt Joints in Steel* and in various other British Standards, some of which are given in Appendix 27. Accounts are given by Kohan (1987) and Pilborough (1989).

X-ray radiography is used during fabrication to detect internal defects, principally in welds but also in the parent material.

BS 5500 requires non-destructive testing by radiography and/or ultrasound for welded joints on Category 1 and 2 pressure vessels. Details are given below.

The X-rays used are produced by an X-ray machine which is relatively immobile and expensive. X-rays are recorded on a photographic plate. In X-ray radiography it is important that there be a high quality image. Standards generally call for a technique which is capable of recording deviations from the normal of not more than 2% of the maximum thickness of the item under test and specify the use of image quality indicators, or penetrameters. Image indicators are dealt with in BS 3971: 1980.

The interpretation of X-ray radiographs is a skilled matter and contains a considerable subjective element. The first step is to identify the type of defect and the second is to quantify it, if quantification is appropriate. The terminology and symbols for weld defects are given in BS 499: 1980 and BS 4727: Part 5, Group 01: 1985. Some of the principal defects that occur in welds are:

(1) planar defects –
  (a) cracks,
  (b) lack of fusion (side, root, interrun),
  (c) lack of root penetration;
(2) cavities –
  (a) porosity (isolated, localized, linear),
  (b) wormholes (isolated, aligned),
  (c) crater pipes,
  (d) surface cavities;
(3) slag inclusions;
(4) other solid inclusions –
  (a) tungsten,
  (b) copper.

Once a defect has been identified, it is necessary to decide whether it is sufficiently serious to require that the weld be rejected. This has again tended to be a subjective matter and has therefore caused considerable difficulty. In consequence, much work has been done to develop acceptance standards. BS 5500 contains a list of defects similar to that given above, together with corresponding acceptance levels.

X-ray radiography is used to detect internal defects in the parent metal, such as in pressure vessel walls, pipework or castings, as well as in welds.

γ-rays are also used for radiography. They are produced by a radioactive isotope source such as cobalt-60. Equipment using γ-rays is portable and relatively cheap. It is used particularly for the radiography of castings. The method is to arrange the castings in a circle with the γ-ray source in the centre and with photographic plates behind the castings. Isotope sources have a relatively large area emitting radiation (usually about 2–6 mm diameter) and therefore tend not to give such good definition as X-rays.

If a permanent record is not required, X-rays may be used with a fluorescent screen instead of a radiographic plate. X-ray fluoroscopy is widely used for the rapid inspection of components on conveyor belts in order to detect coarse defects and unwanted objects. Another technique for rapid inspection is nucleonic gauging of the thickness of materials by passing β-rays through the material.

19.5.3 Ultrasonics

Ultrasonics is another important non-destructive testing technique. This is dealt with in BS 3923: 1972– *Methods for Ultrasonic Examination of Welds*, and the terminology is given in BS 3683: Part 4: 1985. Accounts are given by Birchon (1975), Kohan (1987), Weisweiler and Sergeev (1987) and Pilborough (1989).

Ultrasonics is used during fabrication as an alternative to radiography, to detect internal defects in parent metal and in welds. It is also used to measure thickness. BS 5500 generally gives ultrasonics as an acceptable alternative to radiography for examining welded joints on Categories 1 and 2 pressure vessels.

Ultrasonic waves are generated by a transmitter and detected by a receiver and are usually displayed on an oscilloscope or recorder. Two basic techniques in ultrasonics are (1) transmission and (2) reflection.

In a transmission method the ultrasonic waves are generated by a transmitter on one side of the item under test and are detected by a receiver on the other. The method is shown in Figure 19.1(a).

The reflection method generally uses pulsed waves which are generated by a transmitter and detected by a receiver on the same side of the item. One way in which the method may be applied is shown in Figure 19.1(b), which is known as the A scan. Another application is the B scan, which is shown in Figure 19.1(c). Both these methods give the depth of the defect. A third method is the C scan, shown in Figure 19.1(d), which does not show the depth.

A number of other arrangements for the application of ultrasonics are described by Weisweiler and Sergeev (1987).

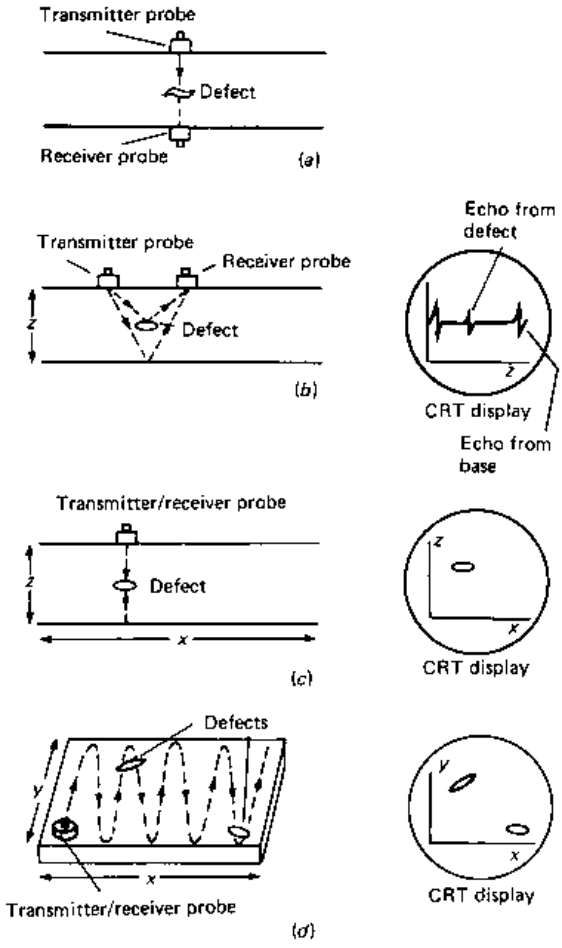

Figure 19.1 *Some ultrasonic testing methods: (a) transmission method; (b) reflection method – A scan; (c) reflection method – B scan; (d) reflection method – C scan*

The beam of waves produced in ultrasonics is not a simple parallel bundle of uniform intensity over the cross-section, and some expertise is required in the interpretation of ultrasonic measurements.

With regard to the choice between radiographs and ultrasonic techniques for welded joints, BS 5500 states:

> Radiographic and ultrasonic methods both have advantages and disadvantages in so far as flaw detection, identification and sizing are concerned. Radiography is particularly suitable for the detection and identification of 'volume' defects such as cavities and solid inclusions and incomplete penetration where a gap exists. Ultrasonic flaw detection is very suitable for the detection and sizing of planar defects such as cracks, lack of fusion and 'tight' incomplete penetration in ferritic steels. The two techniques are therefore to be regarded as complementary and the method chosen which is most suited to the particular application and material. An important consideration is joint geometry which may have an overriding influence on the choice of method. In exceptional cases it may be necessary to employ both methods on the same seam.

Ultrasonics is also used during operational inspections to detect weld defects and to measure thickness.

19.5.4 Magnetic particle methods

A method applicable mainly to surface defects is magnetic particle inspection. This is treated in BS 6072: 1981 *Method for Magnetic Particle Flaw Detection* and in several other British Standards, some of which are listed in Appendix 27. The terminology is given in BS 3683: Part 2: 1985. Accounts are given by Birchon (1975), Kohan (1987) and Pilborough (1989).

Magnetic particle methods are applicable to ferromagnetic materials and are used to detect surface and some subsurface defects. BS 5500 gives magnetic particle techniques as an acceptable method for the testing of welds for surface defects.

There are various methods of magnetic particle testing, but the basic principle is to magnetize the item and coat it with a dry powder of iron or iron oxide particles, or, more usually, a wet powder or 'ink' of particles suspended in kerosene. The particles concentrate at places where there is no continuous magnetic path such as cracks. Defects may then be detected visually. As a further aid to visual detection, a fluorescent substance may be added to the particles and an ultraviolet lamp used. Defects show up best when they are at right angles to the lines of magnetic flux, and it is usual to test the component in two different planes. It is often necessary to demagnetize the item, which is usually done by subjecting it to a magnetic field in the reverse direction to that of the initial one and then gradually reducing the field strength.

19.5.5 Eddy current methods

Magnetic particle methods are applicable only to ferromagnetic materials. An alternative which can be used for the detection of defects in conducting materials, ferrous and non-ferrous, is eddy current testing.

Eddy current testing is dealt with in BS 3889: 1966 *Methods for Non-destructive Testing of Pipes and Tubes* and terminology is given in BS 3683: Part 5: 1965. Accounts are given by Birchon (1975), G. Johnson and McFarlan (1978), Holloway, Bauer and Pittman (1981), Kohan (1987 and Pilborough (1989).

In eddy current testing the item is subjected to an alternating magnetic field which induces eddy currents in it. These induced currents are measured and defects are detected from variations in the current.

Eddy current testing is used principally for the detection of flaws in tubes, both in production lines and on plant. Figure 19.2 shows a defect in a brass tube which passed a 1000 lb/in.^{2} hydraulic test but was detected by eddy current testing.

In the process industries eddy current testing is used particularly on heat exchanger tubes. An account of this application is given by G. Johnson and McFarlan (1978), who describe the testing of tubes by the insertion of a

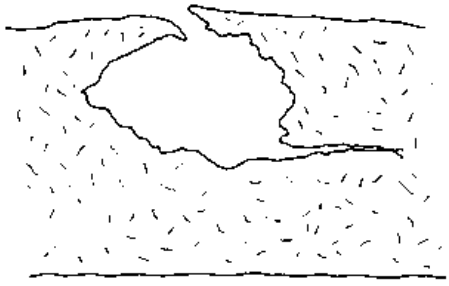

Figure 19.2 *Defect in the wall of a brass tube which had passed a hydraulic test but which was found by an eddy current test (Pilborough, 1989) (Courtesy of Gower Press)*

probe. Defects which can be detected include pitting corrosion and wall thinning.

An account of eddy current testing of furnace and reformer tubes with emphasis on the metallurgical aspects, is given by Holloway, Bauer and Pittman (1981).

19.5.6 Dye penetrant methods

Another method for the detection of surface flaws is dye penetrant testing. This is covered in BS 6443: 1984 *Method for Penetrant Flaw Detection* and the terminology is given in BS 3683: Part 1: 1985. Accounts are given by Birchon (1975), Kohan (1987) and Pilborough (1989).

BS 5500 gives dye penetrant methods as an acceptable method of testing welds for surface defects, and requires this method, rather than magnetic particle testing, to be used for austenitic steels.

The original dye penetrant method was to immerse the item in a heated mixture of paraffin and oil, dry it and clean it, and then dust it with chalk. On cooling the oil seeps out of any cracks in the article and stains the chalk. More modern methods use variations on this, such as special white developer and red dye.

19.5.7 Other methods

There are a growing number of other non-destructive testing methods, such as stress wave emission analysis, holography and electrical resistance methods. In some cases these techniques are used for inspection mainly during fabrication, but in others their application is to operational inspection. Some of the latter are considered in Section 19.11.

19.5.8 Non-destructive testing of welds

The distinction between different categories of pressure vessel is largely based on the extent of the non-destructive testing of welds. For vessels in Category 1, BS 5500 gives the following requirements for the examination of internal flaws:

> The full length of all Type A welds shall be examined by radiographic or ultrasonic methods. Unless otherwise agreed between the purchaser and the manufacturer (see table 1.5), the full length of all welded joints of Type B in or on pressure parts shall be examined by ultrasonic and/or radiographic methods where the thinnest part to be welded exceeds the limits given in table 5.6.4.1.1.

For the examination of surface flaws, the Standard states:

> The full length of all Type B and all other attachment welds shall be examined by magnetic particle or penetrant methods. Type A welds shall be examined by these methods when agreed between the manufacturer, the purchaser and the Inspection Authority (see table 1.5).

For vessels in Category 2 the requirements of the Standard for internal flaws are radiographic and/or ultrasonic examination of 10% of the welds at certain defined locations, the minimum length of weld to be examined at each location being 200 mm or the length of the weld, whichever is the lesser. There are also certain requirements for particular features. For surface flaws the Standard requires examination by magnetic particle and/or dye penetrant methods and states that examination is to be conducted on both of the following:

> (a) the full length of welds attaching nozzles, branches and compensating plates, to shell and end plates; (b) at least 10% of the length of all other attachment welds to pressure components.

For vessels in Category 3 the Standard does not require non-destructive testing for internal flaws unless details producing significant thickness tensile stress are used. Magnetic particle or dye penetratant methods may be used as an aid to visual examination, which is required.

19.5.9 Acceptance standards

It is difficult to overemphasize the importance of acceptance standards. Unless the increasing number of techniques which are capable of detecting defects is matched by the development of standards which define levels of defects below which no action is necessary, there is an obvious danger of unnecessarily frequent rejection.

Much work has been done on the problem by bodies such as the Welding Institute and the American Welding Society, and there is an increasing amount of guidance available.

As mentioned above, BS 5500 lists acceptance levels for certain defects. BS PD 6493: 1980 *Guidance on Some Methods for the Derivation of Acceptance Levels for Defects in Fusion Welded Joints* gives an approach based on fracture mechanics.

19.6 Materials Verification

The fact that, not infrequently, an incorrect material is used in the construction of the plant creates a requirement for inspection to identify such situations. Accounts of material verification are given by Ostrofsky (1980–) and R.J. Sherwood (1989).

The range of tests and instruments available to identify materials is described by Ostrofsky. They include (1) chemical and acid spot tests, (2) tests with tools such as a hammer and chisel or a file, (3) fracture tests, (4) eddy current tests, (5) thermoelectric characterization, (6) spark tests, (7) optical emission spectroscopy and (8) X-ray emission spectroscopy.

The author describes a number of spot tests. A more detailed account is given in *Spot Tests* (Feigel, 1958). Spot tests are also the subject of ASTM STP 550. Ostrofsky also gives details of spark tests, with an

illustration of the characteristic sparks obtained with materials such as low carbon steel, high carbon steel and nickel, and of instruments for field testing which are based on some of these techniques. There are several which utilize optical emission spectroscopy. These include the Metascope referred to earlier.

A programme for verifying the materials installed in the piping of some ten plants is outlined by R.J. Sherwood (1989). Plant sections where the design required materials other than carbon steel were identified; marked-up drawings, pipework tables and inspection procedures were done; access was gained and surfaces prepared; and tests were made using ultrasonics, magnetic particle detection and field analysis instruments.

19.7 Pressure Testing

It is normal to carry out a pressure test on a pressure vessel in order to check that it can be safely operated at the design pressure, but such testing is a potentially hazardous operation. Pressure testing is covered in BS 5500, in the *Pressure Vessel Examination Code* and the *Pressure Piping Systems Examination Code* by the IP (1993 MCSP Pts 12, 13), and also in the ICI *Pressure Vessel Inspection Code* (ICI/RoSPA, 1975 IS/107) and is discussed by Pilborough (1989). Safety precautions are given in these sources and in GS/4 *Safety in Pressure Testing* (HSE, 1992). Also relevant is *A Guide to the Pressure Testing of In-service Equipment* (EEMUA, 1990 Publ. 168).

BS 5500 requires that a pressure test be carried out on any vessel constructed in accordance with the Standard and that the first test should be carried out in controlled conditions with appropriate safety precautions. Adherence to BS 5500 is given in the guidance to the Pressure Systems Regulations 1989 by the HSE (1990 HS(R) 30) as a means of compliance.

The Standard requires that the pressure test procedure should be agreed at the design stage. The test should be performed in the presence of the Inspecting Authority.

19.7.1 Types of pressure test

The types of pressure test given in BS 5500 are:

(1) standard hydraulic acceptance test;
(2) pneumatic acceptance test;
(3) hydraulic proof test;
(4) combined hydraulic/pneumatic test.

A 'standard' test for acceptance is carried out on a pressure vessel where the required thickness of all pressure parts can be calculated. The object of the test is to confirm that the calculated design pressure is a safe working pressure.

If it is not possible to calculate the strength of a vessel satisfactorily, a 'proof' test for acceptance may be conducted to establish a design pressure. In this case the purpose of the test is to determine whether the expected design pressure is a safe working pressure.

In addition to these tests, which are carried out just before or after installation, there are periodic routine tests which are carried out during the operational life of the vessel.

BS 5500 gives certain basic requirements for any type of test. Factors to be considered in the choice of test method include the test fluid and the size and location of the vessel. The procedure should define any areas at risk and the controls to be applied to these.

19.7.2 Standard test pressure

The standard test pressure for a hydraulic, pneumatic or hydraulic/pneumatic test given in BS 5500 is for Category 1 and 2 vessels

$$p_t = 1.25\frac{pf_a t}{f_t(t-c)} \qquad [19.7.1]$$

where c is the corrosion allowance, f_a is the nominal design strength at the test temperature, f_t is the nominal time-independent design strength, or its nearest equivalent, at the design temperature (or the highest temperature at which time-independent strengths are given in the standard, if this is lower than the design temperature), p is the design pressure, p_t is the test pressure, and t is the nominal thickness of the section under consideration. For Category 3 vessels the standard test pressure is that given by Equation 19.7.1) or by

$$p_t = 1.5p \qquad [19.7.2]$$

whichever is the higher. Various qualifications to these test pressures are given in the standard.

Other test pressures are given for proof tests.

19.7.3 Basic test method

Before any test is carried out, the vessel should be given as thorough a visual inspection as is practicable. It may also be desirable to carry out a leak test and, provided that the pressure is not raised to more than 10% of the design pressure, this may be done without the full set of precautions otherwise required for a pneumatic test.

The basic test method described in BS 5500 is to raise the pressure in the vessel gradually to 50% of the specified test pressure and thereafter to increase it in stages of approximately 10% until the test pressure is reached. The test pressure is to be maintained for 30 minutes, except for certain smaller vessels.

The vessel should be inspected during the test for defects, but this needs to be done with care. BS 5500 states:

> At no stage shall the vessel be approached for close inspection until the pressure has been positively reduced to a level lower than that previously attained. The pressure(s) at which the vessel will be approached for close inspection shall be specified in the test procedure. Such pressure(s) need not exceed design pressure but, if in excess of this figure, shall not exceed 95% of the pressure already obtained and held for at least 15 min.

During the test, the vessel should exhibit no sign of plastic yielding.

The test is normally carried out at about ambient temperature. The risk of brittle fracture should be assessed at the design stage. This may affect the choice of material and/or of the temperature at which the test is performed.

There are special test requirements for vessels with multiple compartments.

19.7.4 Hydraulic test

The method of pressure testing preferred in the Standard is the hydraulic rather than the pneumatic method. In

the latter the energy available is large and any failure during the test is likely to be highly explosive. This aspect is discussed in Chapter 17.

For a hydraulic test the test fluid should normally be water, but other liquids may be utilized instead if necessary. If another liquid is used, any appropriate precautions should be observed.

Where hydraulic testing with water is not used, the reasons are generally that the vessel and the structure cannot withstand the weight of water, that the water may be difficult to remove completely or that it may freeze.

19.7.5 Pneumatic test

BS 5500 states that pneumatic testing should only be carried out

> Either on vessels of such design and construction that it is not practicable for them to be filled with liquid, or on vessels for use on processes that cannot tolerate trace liquids and where the removal of such liquids is impracticable.

Testing should only be carried out in consultation with the Inspecting Authority.

Before a pressure test is performed, BS 5500 requires that all welds which have not already been non-destructively tested should be tested by magnetic particle and/or dye penetrant methods.

All suitable precautions should be taken against the hazard of vessel failure. BS 5500 refers in particular to:

> (1) The adequacy of blast protection; (2) the extent of area cleared for test safety purposes; (3) the degree of confidence in stress analysis of vessel details; (4) the adequacy of any non-destructive testing carried out before the test; (5) the resistance of the vessel material to fast fracture; (6) the procedure to prevent local chilling during filling and emptying of the vessel; and (7) the extent of remote monitoring provided during the test.

BS 5500 states that it is permissible to carry out pressure testing with air or gas up to 1.1 times the design pressure on any vessel which has satisfactorily withstood the standard hydraulic, pneumatic or combined hydraulic/pneumatic test.

19.7.6 Proof hydraulic test

In a proof hydraulic test the vessel normally is equipped with strain gauges or is covered with a strain-indicating coating. The pressure is increased gradually until either the standard test pressure for the expected design pressure is reached or significant yielding of some part occurs. From this test the design pressure and a corresponding standard test pressure can be determined. Further details are given in BS 5500.

19.7.7 Pressure testing: safety precautions

The safety precautions to be taken in the pressure testing of pressure vessels are described in GS 4.

The test should be conducted by a competent person. There should be safe systems of work covering *inter alia* the conduct of the test itself and the regular examination of the equipment used in testing, using, respectively, suitable permit-to-work systems and inspection systems. GS 4 details a number of features which should be included in these systems.

All personnel should be kept out of the test area by a system for the control of access. Personnel conducting the test should do so at a suitable distance and with facilities for remote viewing of the vessel.

Hazards which should be considered are the explosion of the vessel and ejection of blanks and plugs, of high velocity fluid jets and of dirt.

Increasingly, pressure vessels under test are monitored for acoustic emissions, this being a prime application of the technique. Further details of the method are given in Section 19.14.

19.7.8 Hydraulic testing: safety precautions

There are various precautions which should be taken before doing a hydraulic test using water. Checks should be made on the effects of static head, on the ability of the vessel and the structure to withstand the weight of water, and on the strength of any temporary pipes, connections or blanks.

The hazard of brittle fracture should be considered. In order to avoid the risk of freezing, the temperature of the water should be not less than 7°C.

If water is used with austenitic stainless steel, it is essential to control the chloride and alkali content. The ICI *Code* specifies the use of demineralized or clean condensate with a chloride content less than 1 ppm.

Measures should be taken to prevent overpressure of the vessel during the test. Accurate and reliable means of measuring the pressure should be provided in the form of a pressure gauge which is freshly calibrated and preferably duplicated. The possibility of overpressure due to water temperature rise and expansion should be considered and, if necessary, a liquid relief valve should be provided. The vessel should have suitable vents so that air can be completely removed. Pockets of air left in the vessel constitute a pneumatic explosion hazard. All filling lines and other equipment which are not intended to be subject to the test pressure should be disconnected before that pressure is applied. Any blanking off devices should be secured so that they will not be ejected during testing.

If a test liquid other than water is used, the hazards should be reviewed. With regard to the choice of liquid, the ICI *Code* states that the liquid should be well below its boiling point and, if flammable, should have a flashpoint above 45°C. The precautions described for water testing are applicable to testing with other liquids.

The test pressure to be applied should be such as not to overstress the vessel. It is normally specified in standards and codes. GS 4 states that in the absence of such guidance the test pressure should be limited to 90% of the proof, or yield, strength. It should be applied gradually in 10% increments.

The vessel under test should not be subject to any form of shock loading such as hammer testing.

19.7.9 Pneumatic testing: safety precautions

As stated, pneumatic testing should be employed only where hydraulic testing is impractical. In particular, pneumatic testing should be avoided if the vessel is constructed of a material that is liable to brittle fracture.

Where the system consists of a number of items which can be tested separately, this is good practice insofar as it minimizes the volume under test, and thus the energy release potential.

If a pneumatic test is to be conducted, a review of the hazards should be undertaken. The vessel should be inspected in accordance with the *Code* requirements, as described above. Inspection requirements are also detailed in GS 4.

Consideration should be given to the possibility of condensation in the vessel, which can defeat the purpose of using pneumatic testing which has been chosen in order to exclude water.

Local chilling effects should be minimized in order to reduce the risk of brittle fracture. A gas let down from high pressure may undergo a significant temperature drop due to the Joule–Thomson effect. A pneumatic test should be carried out in such a way that the temperature of the gas entering the vessel does not fall below the test temperature. Similar considerations apply to gas flows out of the vessel.

If the source of pressure is higher than the test pressure, the vessel should be provided with protection against overpressure by the use of suitable reducing valves, pressure gauges and pressure relief valves.

Where pneumatic testing is conducted using a range of air pressures, positive measures may be taken to ensure that the correct test pressure is applied by arranging that there is for each pressure a different type or size of connection on the air supply, with a corresponding connection on the vessel.

Flexible connections used in pneumatic testing should be firmly secured. Safety restraints may be used to reduce the risk to persons nearby. Equipment used in pneumatic testing, such as pressure relief devices and flexible connections, should be subject to regular examination. Details are given in GS 4. The vessel under test should not be subject to any form of shock loading.

The personnel carrying out the test should be provided with a safe place from which the progress of the test can be observed and controlled. On completion of the test the vessel should be emptied in such a way as not to cause underpressure and collapse.

Underwater pneumatic testing may be employed as a form of a combined pressure test/leak test. The precautions required in such a test are detailed in GS 4.

19.7.10 Multi-compartment vessels

The testing of multi-compartment vessels involves additional hazards and gives rise to fatalities. These tend to occur when a person enters the vessel to inspect leaks from the compartment walls before the strength of the latter is fully tested. Walls may collapse at quite low pressure differentials. Entry should not be made into a multi-compartment vessel for the purpose of leak inspection until the integrity of the compartments has been established by appropriate pressure testing.

19.8 Leak Testing and Detection

19.8.1 Leak testing

Leak testing is carried out to check that a pressure vessel does not have significant leaks at the design operating conditions.

Leak testing is described in BS 3636: 1963 *Methods for Proving the Gas Tightness of Vacuum or Pressurized Plant*, the *Pressure Vessel Examination Code* and the *Pressure Piping Systems Examination Code* of the IP (1993 MCSP Pts 12, 13), the ICI *Pressure Vessel Inspection Code* and by Troyan (1960) and Pilborough (1989). Safety precautions in leak testing are given in these sources and in GS 4 (HSE, 1992).

19.8.2 Pressurization for leak testing

Most leak testing methods involve pressurizing the equipment, although the pressure used may be well below the design pressure. In general, pneumatic leak testing should not be performed until the integrity of the vessel has been established by pressure testing.

It is sometimes desirable, however, to leak test a vessel before a pressure test. As stated above, BS 5500 allows this to be done without observing the requirements for a pneumatic test, providing the pressure during the leak test does not exceed 10% of the design pressure. The guidance given in GS 4 is similar.

Once a pressure test has been carried out, leak testing may be done at pressures in excess of 10% of the design pressure. Nevertheless, the pressure used in leak testing should be kept as low as possible. There is usually little to be gained by the use of high pressures.

The vessel to be leak tested should first be inspected. GS 4 advises that visual examination may need to be supplemented by inspection using non-destructive testing methods.

If a pressure leak test is used and if the source of pressure is higher than the test pressure, the vessel should be provided with protection against overpressure by the use of suitable reducing valves, pressure gauges and pressure relief valves.

As described below, there are methods of leak testing available which do not involve pressurizing the vessel.

19.8.3 Leak location methods

Leak testing is performed for two distinct, but related, purposes: to locate the leak and to determine the leak rate. The main methods used for leak location are:

(1) pressure testing;
(2) search gas methods.

There are a number of leak location methods which involve pressurizing the vessel and then detecting leaks visually. The equipment may be pressurized hydraulically and liquid leaks observed. Detection of leaks may be assisted by the use of some kind of coating which shows them up more clearly. Alternatively, pressurization may be pneumatic and detection effected using a soap bubble or similar technique. If the vessel is sufficiently small to be immersed in a liquid, the evolution of air bubbles may be used to detect leaks in a manner similar to that used in repairing a bicycle inner tube puncture.

Another group of methods is based on the use of a search gas. The gas is introduced into the air pressurizing the vessel and is detected by a suitable device. Some commonly used combinations are:

Search gas	*Detector*
Halogen gas	Halide torch Halogen diode detector
Hydrogen Helium	Thermal conductivity detector
Nitrous oxide	Infrared absorption detector

A variation of this method is to use not a search gas but a radioactive tracer.

Some practical aspects of leak detection are discussed by Troyan (1960).

19.8.4 Leak rate

The leak rate may be defined in terms of the fall in pressure in the vessel

$$L = -V\frac{\mathrm{dP}}{\mathrm{d}t} \qquad [19.8.1]$$

where L is the leak rate ($\mathrm{Pa\,m^3/s}$), P is the pressure (Pa), V is the volume of vessel ($\mathrm{m^3}$) and t is the time (s).

Until quite recently, the internationally agreed unit of leak rate has been the torr l/s ($=0.133\,\mathrm{Pa\,m^3/s}$). Thus in Equation [19.8.1] if, instead of the units given, $V = 1$ l and $\mathrm{d}P/\mathrm{d}t = 1$ torr/s, then $L = 1$ torr l/s. Since this unit is rather large, use has also been made in the UK of the lusec (1 lusec = 0.001 torr l/s). An account of leak rate units is given by Pilborough (1989).

Since the leak rate depends on the difference between the vessel pressure and atmospheric pressure, this should be specified when quoting leak rates. Where the leak rate is for a vacuum plant and the difference is not specified, the assumption is that the pressure difference is 1 atm.

Typical leak rates are given by Pilborough (1971) as follows:

	Leak rate (lusec)
Water can	10
Chemical plant	1
Vacuum plant	0.01

19.8.5 Leak rate methods

The main methods for leak rate determination are:

(1) pressure decay method;
(2) flow method;
(3) search gas flow method.

The pressure decay method is to pressurize the system, isolate it and measure the rate of pressure decrease.

The flow method involves measuring the inlet flow required to maintain the pressure constant.

In the search gas flow method, air is passed over the surface of the equipment and through some form of hood or containment and the flow of air and concentration of search gas in the air are measured.

19.8.6 Leaks in vacuum plant

Leaks are particularly important in vacuum plant. Their detection and measurement is a specialist activity. Accounts are given in texts on vacuum technology and by Pilborough (1989).

19.8.7 On-line leak detection

Methods are also required for the detection of leaks in operating plant. In some cases it is possible to utilize the techniques just described such as the soap bubble, pressure decay and search gas methods.

For high pressure leaks use may be made of acoustic emission monitoring, as described in Section 19.14. For leaks in pipelines another form of acoustic monitoring may be used, as described in Section 19.16.

19.9 Plant Monitoring

The plant equipment, including the pressure vessels and pipework and the process machinery, may be monitored during commissioning and over its operational life.

The monitoring of the state of the equipment may be based on (1) performance or (2) condition. The difference is self-explanatory. Performance monitoring is able to detect faults which have an effect on performance, but there are many others which have little effect until failure actually occurs. The latter may often be detected, however, by monitoring the condition.

The monitoring of instrument performance and condition has been discussed in Chapters 13 and 14 and such monitoring of other equipment is discussed below.

19.9.1 Monitoring strategy

Plant monitoring can yield great benefits, but it can consume appreciable resources. It is essential, therefore, to define clearly the purposes for which such monitoring is to be carried out and to adopt a coherent monitoring strategy.

This is particularly relevant with some types of monitoring, of which acoustic emission monitoring is one, and the point is discussed further below in relation to this type of surveillance.

19.9.2 Monitoring interval

The interval between condition monitoring checks depends on the nature of the signal. If the development of a failure is shown by a slow and reproducible increase in signal level over a long time interval, periodic monitoring may be sufficient, but if the failure gives little advance warning and the signal level is liable to rise from a low to a high level suddenly, then continuous monitoring is necessary.

The problem is one of information sampling and is in many ways similar to that considered in Chapter 14, in relation to the sampling of information by the process operator. Continuous monitoring is generally more expensive and the choice of monitoring interval is usually a compromise between these factors.

Where the quantity monitored is not the state of the plant but changes in that state, as in acoustic emission monitoring, different considerations apply. In this case periodic monitoring, undertaken during changes in the plant state, is the norm.

19.9.3 Action level

The problem of acceptance standards in inspection and non-destructive testing is paralleled by that of the action level for condition monitoring. The decision has two dimensions, since it is necessary to decide not only whether to take action but whether action must be immediate or whether it can be deferred.

A condition monitoring device produces a signal which varies with time. The signal characteristic of normal operation tends to be specific to the individual equipment

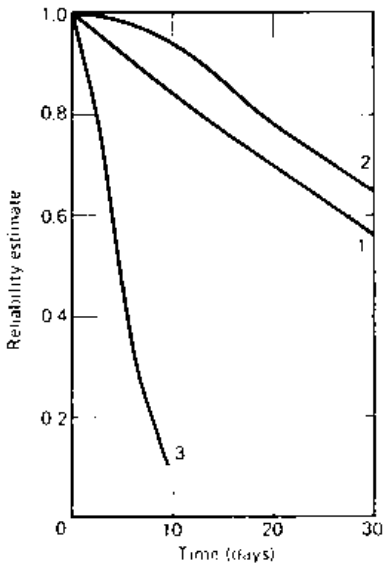

Figure 19.3 *Use of monitor signal to condition the estimate of equipment reliability (Bellingham and Lees, 1976b): curve 1, no monitor signal; curve 2, monitor signal healthy; curve 3, monitor signal unhealthy (Horsley and Parkinson, 1990; reproduced by permission of the Institution of Chemical Engineers)*

monitored. It is a deviation from the equipment's own normal signal rather than from some ideal signal which indicates its abnormal condition.

In many cases there is a fairly reproducible and unambiguous increase in signal level when a failure is imminent. In others, however, the signal is liable to fluctuate, rising to quite high levels and then subsiding, and/or to increase suddenly to failure. There is a considerable problem in these latter situations in deciding whether to take action.

The methods of reliability engineering have been applied to the treatment of the results from condition monitoring. Bellingham and Lees (1976b) describe a method of using the monitor signal to make a running estimate of the probability of survival, i.e. the reliability of the equipment. The method assumes that *a priori* information is available on (1) the failure density function of the equipment and (2) the probability density function of the signal, and uses the signal to condition this information to give the reliability estimate.

An illustrative example of the type of information obtained is shown in Figure 19.3. In the case considered the failure distribution of the equipment is assumed to be exponential. Curve 1 gives the reliability calculated from the failure distribution without using the signal information. Curves 2 and 3 show the reliability estimated from the *a priori* information and the signal for the cases where the signal level is low and high, respectively. The former case indicates a healthy condition and the reliability in the immediate future is high, while the latter case indicates an unhealthy condition and the reliability falls off rapidly.

Applications of the extreme value distribution to the interpretation of results from ultrasonic survey have been described by Wylde and Shaw (1983). One application given is the estimation of the remaining life of a tank wall from measurements of the wall thickness at various points on a corroded band of the wall. Another example quoted is the estimation of the number of deep pits per unit length of pipe from measured values of pit depth.

19.9.4 On-condition maintenance

The various techniques of non-destructive examination and condition monitoring may be used to determine when maintenance should be done on an equipment, as an alternative to either breakdown or scheduled maintenance. This policy is known as on-condition maintenance. An account of on-condition maintenance as a maintenance policy is given in Chapter 7.

19.9.5 On-condition maintenance: illustrative example

Some of the condition monitoring techniques described below involve specialist equipment and sophisticated interpretation. But, as the following example shows, on-condition maintenance may also be based on some very simple measurement.

A maintenance policy for a paper machine has been described by A. Kelly (1981). One component which was prominent in the maintenance was a rotary joint, the main failure being that of one of the seals, which had a life varying between 6 and 30 months. It was realized that the wear on this seal could be determined by measuring the movement of the housing relative to the rotating part of the joint. Thus the condition of the seal could be monitored using a simple measurement of position.

19.10 Performance Monitoring

One basic approach to the surveillance of the health of equipment is to monitor its performance. Typically, performance monitoring is based on the use of a model of the equipment performance with ranges of values of the parameter in the healthy state. These parameters are monitored to detect excursions into unhealthy states. The technique tends to involve the measurement of a number of parameters and to require fairly high measurement accuracy.

Some performances which may be monitored include: (1) the equipment pressure drop; (2) heat exchanger efficiency; (3) the pump characteristic and efficiency; and (4) the compressor, turbine characteristic and efficiency.

Performance monitoring is carried out on large machines such as turbines and compressors in the aerospace, marine, power and process industries. It is usually done to not only to detect failures but also to obtain improved performance. Since performance monitoring generally requires multiple measurement, computation and display facilities, it is a natural task for a process computer.

The performance monitoring of reciprocating compressors by computer has been described by Gallier (1968). The monitoring covered changes in compressor leakage and volumetric efficiency, in compressor and driver power efficiency and in loading capability.

Thus leakage was determined by measuring temperatures and using the equations

$$L = \frac{T_s - T_o}{(T_o + \Delta T_H) - T_i} \quad [19.10.1]$$

$$\frac{T_o}{T_s} = \left(\frac{p_o}{p_i}\right)^{(1-\mu)/\mu} \quad [19.10.2]$$

where L is the fraction of gas leaking, p_i is the suction pressure, p_o is the discharge pressure, ΔT_H is the correction for Joule–Thomson effect, T_i the inlet temperature (before the addition of bypass gas), T_o is the discharge temperature, T_s is the suction temperature, and μ is a constant, approximately equal to the ratio of the gas specific heats.

Collacott (1976b) has described the monitoring of a more complex set of 'gas path' relations in a single spool compressor. A simplified form of the model described is

$$\begin{bmatrix} \Delta P_d \\ \Delta T_d \\ \Delta W_f \\ \Delta A \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{bmatrix} \begin{bmatrix} \Delta T_i \\ \Delta G_a \\ \Delta \eta \\ \Delta N \end{bmatrix} \quad [19.10.3]$$

where A is the jet nozzle exhaust area, G_a the compressor air pumping capacity, N the compressor speed, P_d is the compressor discharge pressure, T_d is the compressor discharge temperature, T_i is the turbine inlet temperature, W_f is the fuel flow, η is the compressor efficiency, and Δ is the normalized increment of the variable (change in value/absolute value).

The performance of the machine is monitored by observing changes in the Δ values of the variables. The method may be summarized as follows. First the coefficients a_{11}–a_{44} in Equation [19.10.3] are evaluated in healthy operation. Then to make a check of machine performance the dependent variables P_d, T_d and W_f are measured at constant speed and the normalized increments ΔP_d, ΔT_d and ΔW_f are calculated. Since the speed is constant, $\Delta N = 0$ and equation [19.10.3] can be evaluated by considering first the top left-hand, third-order matrix. Thus the normalized increments of the independent variables ΔT_i, ΔG_a and $\Delta \eta$ are determined. The normalized increment ΔA is then calculated.

If all the normalized increments are close to zero, there is no performance change. If there is a deterioration, however, ΔG_a, $\Delta \eta$ and ΔT_i normally rise. An increase in ΔA indicates erosion of the nozzle.

Collacott describes the performance monitoring of a power station steam turbine in which there was a sudden reduction in the load, first stage pressure, intercept valve pressure and feed water flow of about 4% in each case. It was decided that there was a restriction at the front end of the turbine. In fact, the stem of one of the four control valves had broken so that the sequence of valve opening was interrupted.

19.11 Condition Monitoring

The alternative to performance monitoring is condition monitoring, for which there is available a variety of techniques.

Accounts of condition monitoring have been given in *Mechanical Fault Diagnosis* (Collacott, 1977b) and *On-Line Monitoring of Process Plant* (D.W. Butcher, 1983) and by Kobrin (1970), Trotter (1973) and D. Neale (1974).

An account of the application of a number of non-destructive testing and condition monitoring techniques to ammonia plants has been given by Madhavan and Sathe (1987).

There are a large and growing number of condition monitoring methods. Some of these are as follows:

(1) vibration monitoring;
(2) corrosion monitoring;
(3) acoustic emission monitoring;
(4) ultrasonics;
(5) infra-red thermography;
(6) strain measurement;
(7) debris analysis;
(8) magnetic signature monitoring;
(9) temperature measurement;
(10) position measurement;
(11) speed measurement;
(12) torque measurement.

There is, therefore, no shortage of methods for condition monitoring. The problem is rather to select the appropriate technique, inspection interval and action level.

The inspection interval depends on the rate at which the fault monitored can develop. There are some faults which can occur within a matter of minutes, while others take weeks or months to develop. Continuous monitoring is necessary to detect faults which develop rapidly.

Whereas non-destructive testing methods are well established and are formally recognized in pressure vessel construction codes such as BS 5500, the role of condition monitoring techniques in inspection codes is generally less well defined.

The use of the process computer for monitoring performance and condition is discussed in Chapter 30.

19.11.1 Vibration monitoring

A widely used method of condition monitoring is the monitoring of vibrations. This is applied mainly to rotating process machinery, but also to static plant equipment. For rotating machinery in particular, it is often possible to relate the vibrations obtained to specific faults in the machine. Since large rotating machines are often critical to the operation of process plants, vibration monitoring has proved an especially valuable aid. It is described in more detail in Section 19.12.

19.11.2 Corrosion monitoring

Another widely practised form of monitoring is corrosion monitoring, which is applied principally to static plant. Corrosion monitoring may be used to track corrosion progressing at a relatively uniform rate and also to identify bursts of intense corrosion activity and to relate these to particular process conditions. The monitoring of corrosion is described further in Section 19.13.

19.11.3 Acoustic emission monitoring

Another monitoring technique which is finding growing application is acoustic emission monitoring, which is applied to static plant and also to leaks. This method is based on the detection of the acoustic emissions which occur as defects undergo changes, notably those accompanying crack growth. It thus differs from most

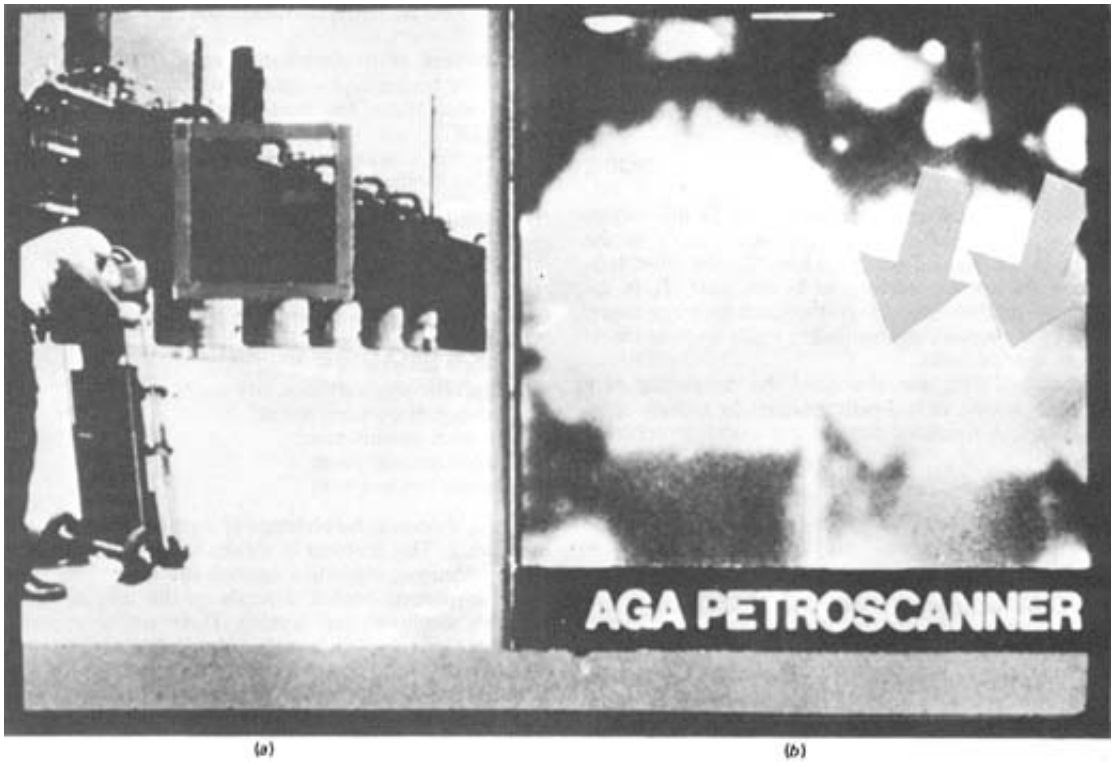

Figure 19.4 *Normal and thermographic photographs of a refractory lined vessel (AGA Ltd): (a) normal photograph; (b) thermographic photograph, with arrows indicating thin spots*

other techniques for monitoring static plant in that it is not the steady state of the defects which are measured but the dynamic changes. A fuller account of acoustic emission monitoring is given in Section 19.14.

19.11.4 Ultrasonics

Ultrasonics is widely used not only for the initial examination of plant equipment, as described in Section 19.5, but also for on-going monitoring. In particular, it is extensively used to determine metal thickness and to identify and characterize cracks in metal structures.

19.11.5 Infrared thermography

An infrared camera can be used to detect differences in the surface temperature of, and hence heat radiation from, plant. The different temperatures may be displayed as different colours or shades of black and white on a cathode ray tube or on a photograph. The technique is known as infrared thermography or thermal image monitoring. Accounts are given by Norda (1976, 1977), L.M. Rogers (1976), Weismantel and Ramirez (1978), Imgram and McCandless (1982), B.G. Jones and Duckett (1985), Tuss (1985) and Baker-Counsell (1986c).
Plate 18 shows the thermal image of a distillation column.

Some applications of thermography are:

(1) refractory and lagging deterioration –
  (a) refractory wear,
  (b) lagging loss,
(2) furnace tube deterioration –
  (a) hot spots,
  (b) coking,
(3) process flow abnormalities –
  (a) heat exchangers,
  (b) steam traps,
  (c) relief valves,
(4) electrical equipment faults –
  (a) cable terminations,
  (b) cable splicing faults,
(5) machinery faults –
  (a) gearboxes,
  (b) couplings,
(6) corrosion.

Thermography has long been used by electrical engineers to detect faults in electrical power systems, but there are now numerous applications in the process industries. Wear of refractories, loss of lagging or moisture penetration of lagging shown up as hot or cold spots. In furnaces, corrosion or other thinning of tubes and coking up of tubes are revealed by temperature changes. The deterioration of flow patterns in a heat exchanger gives a changed temperature pattern. Leaks in steam traps and relief valves which discharge into closed pipelines are shown by a change in the temperature of these lines. Defects in electrical equipment such as bad terminations or cable splicing faults often show up as hot

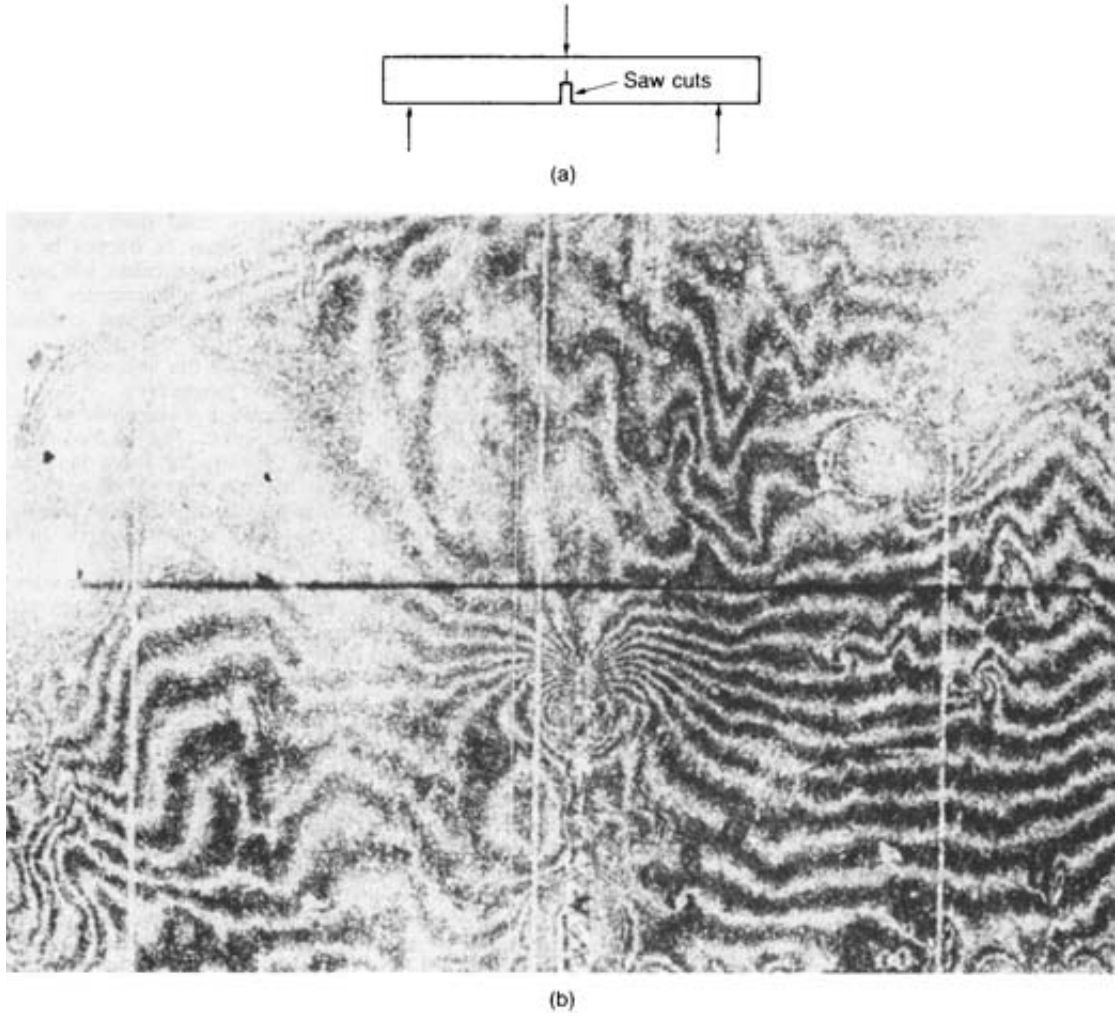

Figure 19.5 Holographic investigation of a fatigue crack: (a) specimen; (b) holographic photograph (*Reproduced with permission of Scottish Technical Developments Ltd and the University of Strathclyde*)

spots. Deterioration of machinery such as couplings or gearboxes tends to generate heat. It is even possible to detect some forms of corrosion.

Figure 19.4 shows a pair of normal and thermographic photographs of refractory lined vessels. The arrows in Figure 19.4(b) indicate areas of one of the vessels where the refractory is wearing thin.

A number of routine applications of thermography in one company are described by Weismantel and Ramirez (1978). These include the detection of leaking steam traps, faults in gearboxes and couplings, and electrical cable splicing defects. Another use described by these authors is to detect leaks beneath the insulation on liquefied natural gas (LNG) tanks.

Imgram and McCandless (1982) describe the use of thermography to detect leaking pressure relief valves. They also describe applications to the deterioration of a catalytic cracker refractory lining wear, a crude heater insulation loss and furnace tube coking. Plates 17(a) and 17(b) show an application similar to the one described by these authors; of the pair of pressure relief valves shown, the one on the right-hand side is leaking.

The application of thermography to the identification of blockages in the relief header of a synthetic rubber plant is described by B.G. Jones and Duckett (1985). The technique used was to pass steam along the line and to observe the thermal transient, blockage points appearing initially as cold spots.

The applications mentioned by Baker-Counsell (1986c) include the use of thermography to detect hydrogen corrosion. The blisters formed cause a decrease in heat transfer and hence, when steam is used, a cold spot.

The main application of thermography is as a method for the normal inspection of the plant, but it may also be

used for other purposes such as the acceptance testing of new equipment.

The distances between the thermal camera and the object may be as much as 100 m or more. Coverage of the temperature range −30°C to 2000°C and accuracies within 1°C are claimed. Thermographic equipment is relatively expensive.

19.11.6 Strain measurement

There are a number of methods of measuring strain in plant equipment. They include

(1) displacement measurement;
(2) strain gauges;
(3) lacquers and coatings;
(4) X-ray diffraction;
(5) interferometry –
    (a) Moiré grid,
    (b) speckle,
    (c) holographic.

Strain may be measured by mechanical displacement or by electrical strain gauges. The latter are widely used as a means of measuring strain in a laboratory, but are rather less suitable for site work. A strain gauge measures strain in one direction only and has relatively low sensitivity. The application of the strain gauge method to the monitoring of steam pipework has been described by Ghia *et al.* (1983).

Photoelastic coatings and brittle lacquers may be used to give an indication of the existence of strain.

Interferometric techniques are available which show a two-dimensional strain pattern and are more sensitive. In the Moiré grid method a linear grid is applied to the object and distortions of the grid are measured.

If the diffusely reflecting surface of an object is illuminated by a laser beam, a speckle pattern is produced. This pattern undergoes regular changes if the surface is displaced by strain. Oxidation of the surface may affect the pattern, but special coatings are available to deal with this problem.

The procedure in the holographic method involves taking a silicone replica of the strained surface and analysing it in a laboratory using a fairly powerful laser (>1 W). Figure 19.5 shows a crack around a fatigue specimen obtained by the Optecord holographic method.

19.11.7 Debris analysis

The debris produced by process machinery in distress may be used to obtain information about the wear which is occurring by using the techniques of debris analysis. Accounts are given by A.E. Davies (1972), Collacott (1975), Wilkie (1987a) and Rudston (1989). The fundamentals of wear are treated by M.C. Shaw (1971).

Debris analysis techniques have been developed primarily in the aerospace and defence fields. Their application is widespread in the transport industry, where debris analysis is utilized for aircraft, marine, rail and road equipment, but its exploitation in the process industries has been somewhat slower.

Debris analysis is closely related to lubrication technology and is also referred to as lubricant monitoring. A monitoring package generally includes analysis of the lubricant itself as well as of the debris which it contains.

The lubricant tests in such a package are fairly standard. They include measurements of: the density of the oil; the viscosity of the oil; the breakdown products of the oil; the contaminants in the oil, such as water and insolubles; the total base number; and the characterization of the metal particles.

The fate of metal particles in the system depends on their size. In essence, large particles (0.1 to <0.5 mm) settle out in the lubricant return tank; medium sized particles (10–50 μm) circulate but may be trapped by a filter; and small particles (1–5 μm) also circulate, but pass through any filter. The filtering arrangements are generally designed to minimize abrasion and erosion from metal particles.

There are two main methods for the analysis of the metal particles: spectrometry and ferrography.

Spectrometric oil analysis involves the analysis of the chemical elements in the oil itself. The method was originally developed by the US Navy Air Force and has been known in the UK as the spectrometric oil analysis programme (SOAP). The method is claimed to be able to detect wear debris at the level of one part in 10^{12} (Collacott, 1975).

Figure 19.6 (A.E. Davies, 1972), shows the wear rates of an Olympus engine in the *Concorde* prototype aircraft as measured by spectrometric oil analysis. Stripping of the engine revealed heavy fret wear on the port gearbox-driven bevel splined location on the lay shaft.

For ferrography, metal particles may be obtained by magnetic chip detection or filter collection. Magnetic chip detection is used in lubricating or hydraulic oil systems to collect debris from ferromagnetic materials. The detector is periodically examined and the debris analysed. The use of magnetic chip detectors is quite widespread in the process industries. Filters in oil systems are also used to collect debris particles for analysis.

In the aircraft industry the analysis of debris is a well developed technique. Filter elements are removed under conditions of almost clinical cleanliness and the debris is examined by microscope and analysed chemically. Samples of filter washings are preserved under transparent covers on record cards.

Some typical normal and alert wear/corrosion ranges given by Rudston (1989) are as follows:

	Spectroscopic metals		*Ferrographic readings*	
	Ferrous	*Non-ferrous*	*Large debris*	*Small debris*
Rotating machinery	≥8 (0–5)	≥8 (0–5)	≥15 (0–5)	≥2 (0–0.5)
Reciprocating machinery	≥150 (0–100)	≥20 (0–15)	≥120 (0–100)	≥40 (0–30)

The values shown without brackets are alert values and those shown in brackets are normal values. These provide a general guide, but monitoring of a given machine is usually based on deviations from the previous pattern shown by that machine.

Table 19.11 *Some typical characteristics of metal particle debris in lubricating oil*

A

Conditions	*Particle appearance*
Running in	Feathery or flaky
Roller bearing distress	Heavy rectangular shape with regular crossing marks (team lines)
Ball bearing distress	Shiny, roughly circular, petalled chips

B

Damage process	*Particle type*	*Surface appearance*
Mild wear (delamination)	Small flat reflective flakes	As machined but with more plateau area
Adhesion/ scuffing	Larger ragged flakes often with temper colours	Rough and torn
Abrasion/cutting	Bright slivers and curls	Scratched and scored
Fatigue	Sharp metallic chunks and small spheres	Cracked and spalled
Erosion	Bright chunks or spheres	Pits or grooves with rough surface
Fretting	Fine red-brown iron oxide	Localized staining or indentation
Corrosive wear	Powdery non-reflective deposit	Fitted and discoloured

Sources: Collacott (1975); Rudston (1989)

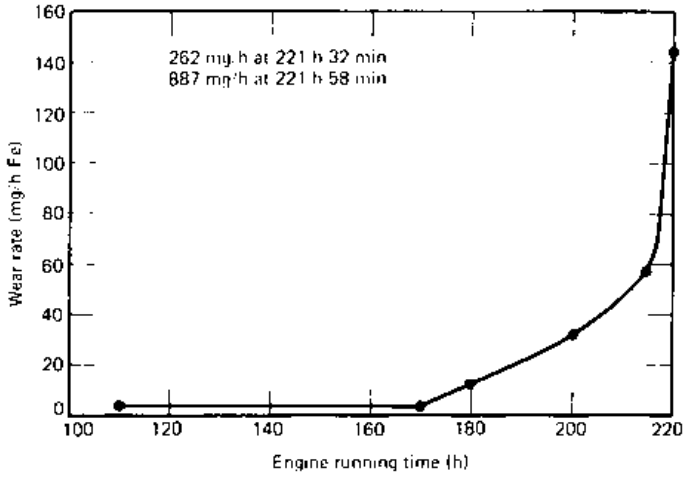

Figure 19.6 *Trend record of a spectrometric oil analysis on an Olympus 59332 engine in the* Concorde *prototype aircraft (A.E. Davies, 1972) (Courtesy of the Institution of Marine Engineers)*

Particular wear processes tend to give characteristic particle shapes and much can be learned by examining the particles under a microscope. Some typical debris characteristics are shown in Table 19.11.

19.11.8 Other general methods

Other methods which are used to monitor condition include the measurement of conventional variables such as temperature, position, speed and torque, and magnetic field measurements.

Temperature is used in particular to monitor plain bearings. It is not so good an indication for ball bearings, however.

Blades of rotating machinery such as turbines or fans may be magnetized or, if made of non-magnetic material, may be seeded with a magnetic implant. The 'magnetic signature' caused by the rotation of the magnetized part may then be monitored by a magnetic sensor.

There are numerous other physical phenomena which may be made the basis of a method of condition monitoring. Barnhart (1963) has listed some 387 physical laws and effects.

19.11.9 Specific *ad hoc* methods

In addition to the general methods described, there are a number of *ad hoc* methods for monitoring specific items of equipment. A good illustration of such methods is the rotary joint application described in Section 19.9.

Two further examples will suffice, one on pumps and one on valves. The first is the work of D. Harrison and

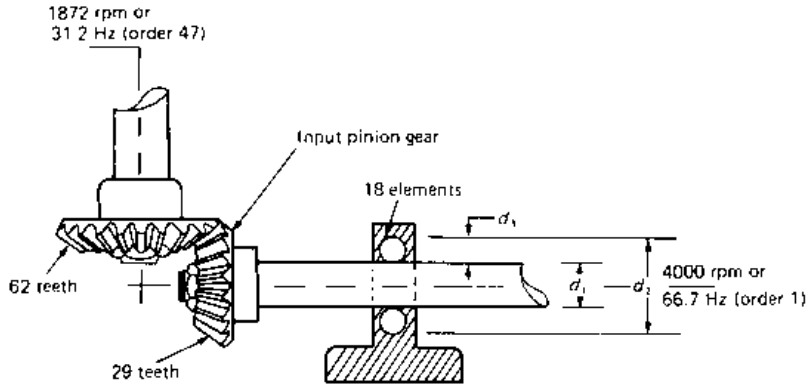

Figure 19.7 Pinion gear assembly (Fieldhouse, 1970) (*Courtesy of Sound and Vibration*)

Watkins (1983) on instability in pump mechanical seals, prompted by severe difficulties on main oil line pumps offshore. The problem involves vaporization between the seal faces of the pumped fluid which normally lubricates the seals. The authors describe the measurement of the seal leak chamber pressure as an indicator of the onset of instability.

D. Harrison and Heath (1983) have described work on the use of changes in valve torque as a measure of incipient failure to achieve the fully open or closed position.

19.11.10 Adaptive noise cancellation

In many monitoring applications there is an appreciable degree of background noise. One technique which has been developed specifically to deal with this problem is that of adaptive noise cancellation (ANC), described by Widrow *et al.* (1975).

An account of the application of ANC to the monitoring of rolling element bearings has been given by Tan and Dawson (1983).

19.12 Vibration Monitoring

Vibration monitoring is described in *Mechanical Fault Diagnosis* (Collacott, 1977b) and *Mechanical Vibration and Shock Measurements* (Broch, 1980) and by Fieldhouse (1970), Tustin (1971), F.G. Jones (1971), C. Jackson (1975–), Erskine (1976a,b), Goldman (1984) and Goggin (1987).

19.12.1 Machine vibration

Much information on the condition of machinery can be obtained by monitoring vibrations. Monitoring needs to be combined with a theoretical analysis of the vibration modes so that particular faults can be distinguished.

Accounts of vibration include *Vibration and Sound* (Morse, 1936), *Mechanical Vibrations* (den Hartog, 1956), *Engineering Vibrations* (Jacobsen and Ayre, 1958), *Shock and Vibration Engineering* (C.T. Morrow, 1963), *Structure-Borne Sound* (Cremer and Heckl, 1973), *Vibration Problems in Engineering* (Timoshenko, Young and Weaver, 1974), *Elements of Vibration Analysis* (Meirovitch, 1975), *Shock and Vibration Handbook* (C.M. Harris and Crede, 1976) and *Mechanics of Vibration* (Bishop and Johnson, 1979).

Broch gives an account of vibration and shock which covers its characterization, the response of mechanical systems to it, its effect on mechanical systems, its measurement, its analysis, and its use for machinery health monitoring.

As an illustration, consider the pinion gear assembly described by Fieldhouse (1970) and shown in Figure 19.7. The analysis given by this author of some of the frequencies of vibration generated by this mechanism is summarized in Table 19.12.

Numerous other analyses of the modes of machine vibration are available.

19.12.2 Vibration quantities

Vibration quantities that are measured are (1) displacement, (2) velocity and (3) acceleration. Each quantity is measured using a different type of transducer.

Displacement measurement is utilized for detecting the change in clearances. It is particularly useful on reciprocating machines. It discounts and is not suitable for high frequencies (>1000 Hz).

Velocity measurement is a commonly used method for both machines and structures. It gives equal weighting to both low and high frequencies, since it is the product of the displacement and frequency of each harmonic component.

Acceleration measurement is useful for detecting impact effects. It discounts and is not suitable for low frequencies.

The choice of vibration quantity and measurement device is discussed by Broch (1980). There has been a trend towards higher frequencies, and measurements may be made at 10 Hz or higher. Broch's account emphasizes the use of accelerometers, with velocity or displacement obtained by integration.

Table 19.12 *Some frequencies arising from a pinion gear assembly (after Fieldhouse, 1970) (Courtesy of Sound and Vibration)*

Assembly parameters:			
No. of teeth on input gear, N_1	29		
No. of teeth on output pinion, N_2	62		
Diameter of inner race, d_1	3 in.		
Diameter of outer race, d_2	4 in.		
Diameter of balls, d_3	0.5 in.		
Number of balls, N	18		
Speed of rotation of input shaft, n_1	4000 rev/min		
Constant D_1 $(= d_1/(d_1 + d_2))$	0.428		
Constant D_2 $(= d_2/(d_1 + d_2))$	0.572		
Assembly frequencies:		Hz	Order
Frequency of rotation of input shaft, f_{n1}		66.7	1
Fundamental gear mesh frequency, f_{gm} $(= f_{n1}N_1)$		1934.3	29
Frequency of rotation of output shaft, f_{n2} $(= f_{gm}/N_2)$		31.2	0.47
First upper sideband of gear mesh frequency, f_u $(= f_{gm} + f_{n1})$		2001	30
First lower sideband of gear mesh frequency, f_l $(= f_{gm} - f_{n1})$		1867.6	28
Differential frequency of rotation of inner and outer races, f_r $(= f_{n1})$		66.7	1
Frequency of ball spin, f_s $(= f_r D_1(d_2/d_3))$		228	3.4
Frequency of ball train passage, f_t $(= f_r D_1)$		28.5	0.43
Frequency of flaw on inner race, f_{f1} $(= f_r N D_2)$		687	10.2
Frequency of flaw on outer race, $f_{f2}(= f_r N D_1)$		514	7.7
Frequency of flaw on ball, f_{f3} $(= 2f_s)$		456	6.8

The units of measurement commonly used are

Displacement	μm	mil
Velocity	mm/s	in./s
Acceleration	m/s^2	ft/s^2

There are also several different signal quantities which may be measured. These are (1) peak, (2) peak-to-peak, (3) average, and (4) root mean square (rms). All these quantities are used in the various instruments currently available for the measurement of the vibration quantities (displacement, velocity and acceleration).

The peak and peak-to-peak values give, respectively, the peak vibration loading and the swing in loading; the average and rms values give, respectively, the average vibration loading and the power in the loading. The peak and peak-to-peak values are dependent on the waveform, but the average and rms values are not.

The peak vibration velocity is the quantity generally considered to be the most useful signal by some authors (e.g. Erskine, 1976a). If a peak value is required, it is important to ensure that a true peak reading meter is used, as described below.

Alternatively, the full power spectrum of the signal may be produced. Spectral analysis instruments are available to generate the power spectrum.

An illustrative example showing the value of signal filtering is given by Goldman (1984). He considers the monitoring of a gear box which has a mesh frequency of 1 Hz and an outer race ball pass frequency of 236 Hz. Typical signals might be:

	Velocity (in./s)		
Week	*Overall*	*Mesh* (1 Hz)	*Bearing* (236 Hz)
1	0.1	0.1	0.01
2	0.1	0.1	0.02
3	0.1	0.1	0.03
4	0.1	0.1	0.04
5	0.11	0.0	0.05

Measurement of the strength of the overall signal would show relatively little change, but separate measurement of the mesh and bearing signals would show the bearing beginning to fail at about week 3 and being close to failure by week 5.

19.12.3 Vibration measurement

The instrumentation used for vibration monitoring consists of a transducer, a signal conditioning amplifier and a readout meter. The transducer may measure displacement, velocity or acceleration directly. Alternatively, acceleration may by integrated to give velocity, and velocity to give displacement. An account of vibration measurement is given by Broch (1980).

The function of the amplifier is to give a larger power signal and to transform it into the signal quantity required. Many instruments scaled for peak, peak-to-peak or rms values in fact read the average value. The

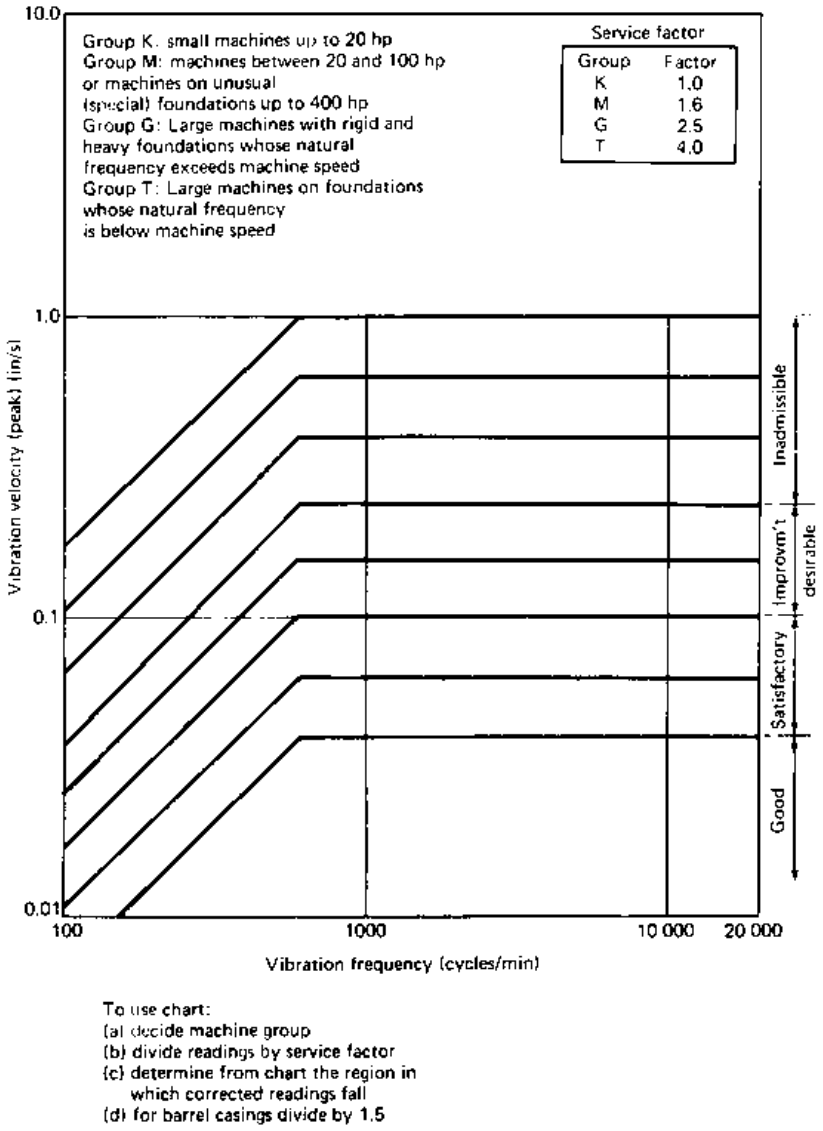

Figure 19.8 *Vibration criteria for process machinery (Erskine, 1976a) (Courtesy of the Institution of Chemical Engineers)*

different types of circuitry are described by Erskine (1976a).

There are a number of practical aspects which need to be observed if satisfactory results are to be obtained in vibration monitoring work. On each occasion the measurement should be taken at the same point and in the same direction. Therefore, if a portable monitor is used it is useful to indicate the point with a small circle of white paint with a small hole drilled in the centre. The tendency for a portable transducer to bounce can be overcome by the use of a 'mole' wrench as a clip. The same instrument should always be used to take a given reading, since instruments which ostensibly read the same parameter may in fact have different internal circuitry. The transducer should be calibrated at intervals of 18 months or less and the instruments at intervals of 3 months.

As far as possible vibration measurements should be made under the same machine conditions. Some variable speed machines have a rotor critical speed within the

operating range, although the machine should not be operated at this speed. If it is being so operated, the additional vibration detected is an indication of maloperation rather than malfunction.

19.12.4 Vibration criteria

For rotating process machinery such as turbines, compressors, pumps and fans there are some general guidelines available to determine the level of vibration at which action is required, i.e. the vibration criteria. Early vibration criteria were those proposed by Yates (1949) and Rathbone (1963). A widely used set of vibration criteria is that of the IRD, the details of which are quoted by Collacott (1977b).

One of the most widely used guidelines for general process machinery is that given in VDI 2056: 1964 *Standards for Evaluation of Mechanical Vibration of Machines.*

Criteria for the balancing of machines are given in ISO 1940: 1986– *Mechanical Vibration–Balance Quality Requirements for Rigid Rotors*, ISO 2371: 1974 *Field Balancing Equipment: Description and Evaluation*, ISO 2953: 1985 *Balancing Machines: Description and Evaluation* and ISO 3945: 1985 *Mechanical Vibration of Large Rotating Machines with Speed Range from 10 to 20 r/s: Measurement and Evaluation of Vibration Severity in situ.*

Vibration criteria, both for independent bearings and for bearing housings in barrel casings, which have been developed from the VDI method and used in ICI, have been described by Erskine (1976a) and are given in Figure 19.8. The quantity used is the peak vibration velocity, which has the advantage that it is independent of the machine speed and vibration frequency. Experience also indicates that Figure 19.8 can be used for gearboxes if they are treated as Group T.

These vibration criteria provide general guidance. In practice, it is usual to take an initial baseline set of measurements on the particular machine and thereafter to monitor the trend on that machine.

Another useful source of information for comparison may be the vibration levels on similar machines in a group.

Use may be made of certain rules of thumb. Goldman refers to the rule that a doubling of the signal strength is an indication of trouble, whilst a trebling is cause for concern.

19.12.5 Shock pulse monitoring

A particular type of vibration monitoring which is based on selective filtering is shock pulse monitoring. The shock pulse meter exploits two facts. One is that at the natural frequency of a mounted accelerometer a large electrical output can be obtained from a small excitation. The other is that an instantaneous impact gives a signal which contains all frequencies at equal amplitude, in other words white noise. Thus the signal given by an impact will contain the frequency required to excite the accelerometer. In a shock pulse meter the signal at this frequency is amplified by the accelerometer, filtered and then measured.

The main application of the shock pulse meter (SPM) is the monitoring of faults in ball bearings. If, for example, a single spall develops in the outer race, an impulse occurs each time a ball passes over the spall. As deterioration occurs, the level of white noise, and the signal from the meter, should increase.

In practice there are certain problems which can arise. There may be sources of white noise which are unrelated to the defect and, as the defect grows, the signal generated may no longer be white noise. The situation can occur where the meter signal actually reduces as the deterioration progresses.

An enhancement of the SPM technique is the use of a stress wave analyzer (SWAN), which exploits the fact that the amplitude of the impulse is proportional to the relative velocity between the two bearing surfaces and to the depth of the imperfection, and gives a signal proportional to the area of the bearing fault.

Table 19.13 *Frequencies detected for some common process machinery faults*

Fault	*Frequency*[a]
Oil whirl	$\frac{1}{2} \times N$
Unbalanced, eccentric journals	$1 \times N$
Misaligned shaft	$1 \times N$
Aerodynamic forces (fan)	$1 \times N$
Reciprocating forces	$1, 2... \times N$[b]
Bent, cracked shaft	$1, 2 \times N$[c]
Misalignment of couplings or bearings	$1, 2, 3 \times N$[d]
Mechanical looseness	$1, 2, 3, 4 \times N$[e]
Defective gear	$n_g \times N$
Blade defect	$n_t \times N$
Failing coupling	$n_c \times N$
Defective belt drive	$1, 2, 3, 4 \times n$b
Defective bearings	Very high, several times N
Defective mountings (soft foot)	$1, 2 \times N$[f]
Structural resonance	$1 \times N$[g]

Sources: Lees (1980b); Goldman (1984); Goggin (1987).
[a] N, the rotational speed of the machine (rpm); n_b, the rotational speed of the complete belt; ng, the number of gear teeth; n_t, the number of blades
[b] $1, 2 \times N$ and higher orders.
[c] Goldman gives $2 \times N$; Goggin gives $1 \times N$, or $2 \times N$ if bent at coupling.
[d] Goldman gives $2 \times N$; Goggin usually gives $1 \times N$, sometimes $2, 3 \times N$.
[e] Goldman gives $1, 2, 3, 4 \times N$; Goggin gives $1, 2, 3 \times N$.
[f] Usually $1 \times N$, sometimes $2 \times N$.
[g] $1 \times N$, but often odd non-synchronous frequency.

19.12.6 Plant applications

Vibration monitoring can be applied both to rotating machines and to static plant. The quality of information which can be obtained goes far beyond the detection of the fact that something is wrong, and it is often possible to pinpoint the fault quite precisely.

Some typical information given by vibration frequencies, particularly those which are multiples of the speed of rotation, is shown in Table 19.13.

Figure 19.9 illustrates time histories and power spectra of vibration signals for some typical rotating machine conditions.

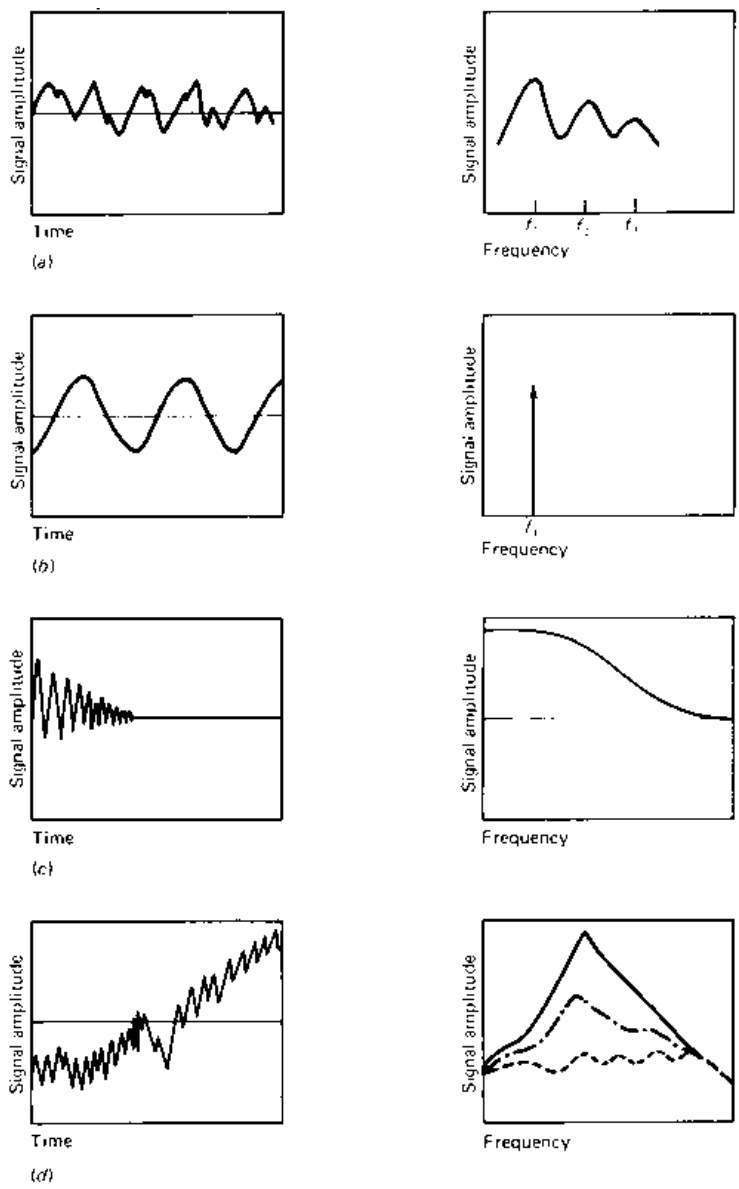

Figure 19.9 *Trend records and power spectra of some typical machine conditions (Collacott, 1975): (a) normal operation; (b) imbalance; (c) shock; (d) impending major failure*

Vibration methods can also be applied to static plant such as distillation and gas absorption columns and heat exchangers. Figure 19.10 shows the power spectrum of a heat exchanger under normal and abnormal conditions.

In many cases the level of vibration at a particular frequency or frequency range is low, unless there is an abnormal condition. In such cases arrangements can be made to filter out all other frequencies so that the level of signal retained is an unambiguous indication of the abnormality. Thus for the heat exchanger shown in Figure 19.10 a suitable filter is one which retains only frequencies in the range 250–750 Hz. The resultant signal can then be used to indicate heat exchanger rattling.

19.12.7 Monitoring policy

There is now considerable vibration monitoring activity in process plants. Some machine conditions are monitored by permanent instruments, others are checked by portable meters. On critical items such as turbines, compressors and large pumps there is a high proportion

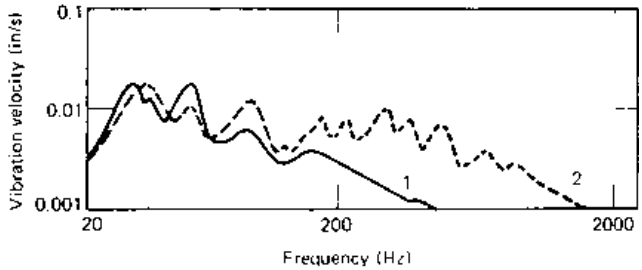

Figure 19.10 *Power spectrum of a heat exchanger (Erskine, 1976a): curve 1, exchanger quiescent; curve 2, exchanger rattling (Courtesy of the Institution of Chemical Engineers)*

of continuous monitoring with alarms and trips. These machines are also the subject of further spot checks and of sophisticated spectral analysis by specialist staff. For other less critical machines spot checks by less skilled personnel using portable meters are often sufficient.

An account of monitoring policy is given by Goldman (1984). Continuous monitoring is likely to be appropriate if (1) the machine is critical to production, (2) it is costly to replace and/or (3) its failure would be hazardous. Periodic monitoring may be carried out on machines where (1) the machine is moderately important for production, (2) its replacement is costly, (3) it is a major machine but is spared, or (4) it has a poor operating history.

The vibration criteria at which action is required depend on the application. For meter checks by unskilled people it is essential to have very simple criteria, while specialist personnel may base their decisions on much more complex analysis.

19.13 Corrosion Monitoring

There are available a number of methods for the monitoring of corrosion, both on-line and otherwise. Accounts of corrosion monitoring are given in *Industrial Corrosion Monitoring* (Hines, 1978) and by Harrell (1978), Rothwell (1979), Strutt, Robinson and Turner (1981), Asher *et al.* (1983), Dawson, Eden and Hladky (1983), Robinson and Strutt (1983) and M. Turner and King (1986).

Corrosion monitoring may be undertaken for a variety of reasons. It may be used to (1) inspect for corrosion and, in particular, give early warning of severe corrosion, and to (2) diagnose a problem, (3) monitor a solution to a problem, (4) correlate the corrosion regime with the plant operating conditions, (5) monitor the operation of the plant and (6) control the operation of the plant.

Corrosion is a complex phenomenon. This is so even under the controlled conditions of the laboratory and even more so on an operating plant. Corrosion has a number of causes and it is not advisable to place total reliance on a single method.

Some corrosion monitoring techniques identify the corrosion regime in the plant, whilst others indicate or measure the corrosion actually occurring. Taking the latter first, some principal methods are visual inspection, coupon testing and sentinel holes.

Visual examination requires access and is used particularly at shut-downs. There is a variety of aids to visual examination, including closed circuit TV and optical techniques. Coupon testing involves locating a sample element in the equipment and measuring the degree of corrosion of the element. A sentinel hole is a hole drilled through from the outside to a point close to the internal surface, so that it will leak if significant internal corrosion occurs.

Some authors include among the techniques of corrosion monitoring non-destructive testing methods such as radiography, ultrasonics, eddy current testing, acoustic emission testing and thermography.

Electrochemical methods of corrosion monitoring are described by Strutt, Robinson and Turner (1981). These methods are used for investigating the corrosion regime and include (1) chemical analysis, (2) the corrosion potential method, (3) linear polarization resistance (LPR), (4) electrochemical impedance, (5) potentiodynamic scans (PDSs) and (6) electrochemical noise.

The LPR, electrochemical impedance and PDS techniques all involve the investigation of current and voltage using a set of probes. The main difference between them is the form of input signal to the probe and the analysis performed on the output.

Electrochemical methods are best suited to providing early warning of corrosion behaviour and to correlating the corrosion regime with the operating conditions.

The control of electrochemical corrosion measurements and the display of data in various forms is a natural application for a microprocessor. The authors illustrate a number of plots which may be displayed, including trend charts, scatter diagrams, control charts, polarization diagrams and Nyquist diagrams. A polarization diagram is a plot of potential vs current and a Nyquist diagram a plot of resistance vs reactance over a range of frequencies.

An overview of corrosion monitoring methods is given by Rothwell (1979), who tabulates for each technique the type of information which it yields, the type of corrosion for which it is suitable, the environment in which it may be used, the time taken for the measurement to be made, the response to changes in corrosion, the application of the technique to an operating plant, and the ease of interpretation.

A method widely used to measure the actual rate of corrosion is coupon testing. The corrosion of the coupon

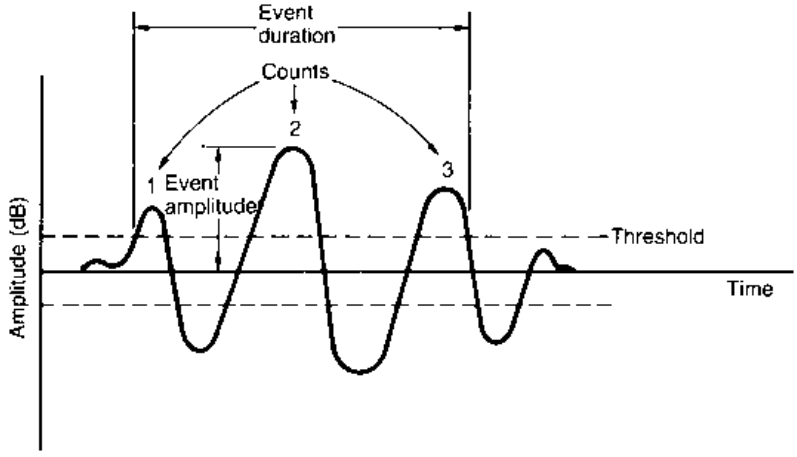

Figure 19.11 *A typical signal from an acoustic emission test*

may be measured gravimetrically by periodically removing and weighing it. It is important to locate the coupon so that it is representative of the corrosion to be monitored. It should generally be flush and in continuity with the vessel or pipe unless it is specifically desired to measure local corrosion/erosion effects. The choice of element size is a compromise between measurement sensitivity and replacement frequency.

The coupon testing method may be adapted to form the basis of an instrument for the measurement of the corrosion rate. The electrical resistance of the sample element increases as its cross-sectional area decreases and thus provides a measure of the cross-section remaining. Since the electrical resistance is sensitive to temperature, corrosion meters need to be temperature-compensated by using a reference element which is not exposed to corrosion. The corrosion rate is obtained by differentiating the reading of a corrosion meter.

The current in an electrical resistance corrosion meter is appreciable. For use in a hazardous area the intrinsic safety of the system may need to be checked.

Another technique for the measurement of the corrosion rate is radioactivation, as described by Baker-Counsell (1985g). This involves making mildly radioactive the surface which is subject to corrosion and measuring the change in radioactivity. In the thin layer activation version of this method only a thin layer at the surface is activated. This has the advantages that the sensitivity of the measurement is high and the radioactivity so low as to obviate the need for taking any special precautions against it.

Typical corrosion rates are of the order of 10 mil/year (1 mil = 0.001 in.), but rates can vary widely and, in particular, under certain process conditions may accelerate dramatically.

Examples of the use of corrosion monitoring are given by Rothwell (1979). Case histories are described by Harrell (1978). A detailed account of the monitoring of a standard corrosion experiment, the corrosion behaviour of 316 stainless steel in 0.1 M NaCl, is given by Strutt, Robinson and Turner (1981).

Another method of monitoring corrosion and erosion is to measure the wall thickness by using ultrasonics. The use of ultrasonics in this application, and in particular as a method of obtaining results reproducible enough to track the progress of any thinning, is described by Browne and Constantinis (1983).

19.14 Acoustic Emission Monitoring

Many physical phenomena are associated with the emission of noise. Examples are the creaking of the branch of a tree and the 'cry' of tin. Acoustic emissions may be picked up by a microphone and used to monitor both pressure vessels and process machinery.

Acoustic emission (AE) monitoring is dealt with in *Mechanical Vibration and Shock Measurements* (Broch, 1980), the two IChemE guides described below, and by McFarland (1970), Witt (1971a), Fowler and Scarpellini (1980), Cole (1983, 1988, 1990, 1992), L.M. Rogers and Alexander (1983), Treleaven (1983), Fowler (1986, 1987, 1988, 1992), Pollock (1986), Clough (1987), Heiple and Carpenter (1987), Frieshel and Jones (1988), Prasek (1988), Zhang (1988) and Hewerdine (1991).

The earlier guide published by the IChemE, *Guidance Notes on the Use of Acoustic Emission Testing in Process Plants*, was prepared by a working party of the International Study Group on Hydrocarbon Oxidation (ISGHO) (1985), and the current guide, *Plant Integrity Assessment by Acoustic Emission Monitoring* (Hewerdine, 1993) (the IChemE *AE Monitoring Guide*), was prepared by the International Process Safety Group (IPSG), the successor to the ISGHO.

19.14.1 AE sources

When a defect undergoes change, such as a crack experiencing growth, there is a release of energy, part of which is converted to elastic waves. This acoustic energy may be detected, and this forms the basis of AE monitoring. Some principal AE sources are crack growth, corrosion product fracture and local yielding.

19.14.2 AE signals

An acoustic emission occurs when a defect in a metal plate is put under stress. An elastic stress wave travels through the plate. The measurement of this wave is the basis of the AE technique. The emissions of interest occur in 'bursts', each burst being known as an event. Figure 19.11 illustrates a typical AE event. The start of the event occurs with the initial signal at arrival time t_o. There then occur a number of excursions, or counts, outside the set threshold. The event is characterized by the arrival time, the duration, the number of counts and the amplitude of the largest count, or maximum amplitude.

An acoustic emission is not emitted on all occasions when a defect is put under stress. It was held in early work that an emission occurs only when the stress is taken to a value higher than that previously applied. This is the Kaiser effect and it assumes that the energy release is irreversible. Later work showed that this was not the whole story, and that if a sufficient recovery period is allowed the emissions can again be obtained at lower stresses. This disappearance of the Kaiser effect is known as the Felicity effect. The significance of this is that if the fading of the Kaiser effect did not occur, it would be possible to use AE monitoring only for applications where a vessel was subject to successively higher pressures, which would be a severe limitation.

Different materials exhibit different AE characteristics and in order to apply the technique it is necessary to establish these. AE monitoring has been applied *inter alia* to carbon steel, stainless steel and fibre reinforced plastic (FRP) equipment.

19.14.3 AE measurement

A typical set-up for the AE monitoring of a vessel is a set of three or more probes. By using a set of three probes to give 'triangulation' and utilizing the travel times of the emission waves measured by the probes, it is possible, in principle to locate the source of the emission.

There are in fact a number of practical problems in doing this: the level of background noise; interference between one event and another; the assumption that the stress wave travels at a constant, known velocity; and the calibration of the AE equipment.

The assumption of a constant stress wave velocity applies to flat steel plate. There are differences in velocity for waves in flat steel plate and in the curved walls of vessels. Also, the different frequency components travel at different velocities.

An approach based on zone location rather than source location, described by Fowler (1987), attempts to overcome some of these difficulties.

19.14.4 AE signal analysis

Early approaches to AE monitoring concentrated primarily on the location of defects. More recent work has extended this to the characterization of the parameters of the signal and of the defects. To this end extensive use is made of computer processing of the signals obtained.

19.14.5 AE monitoring characteristics

AE monitoring is therefore a technique for detecting the occurrence, and measuring of the magnitude of, dynamic changes occurring in defects rather than of the static defects. This is a fundamental difference between AE monitoring and conventional non-destructive testing (NDT) methods. It has a number of implications.

One is that AE signals occur only whilst changes are taking place. Thus AE monitoring is typically conducted on a periodic basis, when plant loading is being altered, rather than continuously.

Another consequence is that a site which gives a signal detectable by AE monitoring may not give one detectable by NDT methods, and vice versa. AE monitoring can detect cracks which are growing, even though they may still be small, whereas NDT detects only larger cracks. On the other hand, the AE technique may not detect even such larger cracks unless they are experiencing growth at the time when the measurements are made.

Since AE methods give information on defect changes they complement well the techniques of fracture mechanics described in Chapter 12.

AE has the advantage that it is a global monitoring technique which allows the whole of a structure or vessel to be monitored. This distinguishes it from many NDT methods, such as ultrasonics or eddy current testing, which inspect a limited area. Furthermore, AE monitoring requires only limited access to the equipment and allows remote detection and location of flaws

Limitations of AE monitoring are that: the structure has to be loaded; the source activity is highly dependent on the material; there may be interference from noise; the interpretation of the results can be difficult; the location of the flaw may not be very accurate; and identification of the type of defect may not be readily made.

19.14.6 AE monitoring standards and codes

There are a number of standards and codes applicable to AE monitoring. ASTM standards include: ASTM E 569–91E1, giving general guidance; ASTM E 1067–89, on FRP tanks and vessels; and ASTM E 1211–87, on leak detection.

Treatments proposed by the American Society of Mechanical Engineers (ASME) include those on the use of AE in lieu of radiography (1982), FRP vessels (1983) and on metallic pressure vessels (1989).

The Society of the Plastics Industry (SPI) (1987) has also issued a recommended practice for FRP tanks and vessels.

Rail tank car monitoring is covered by a procedure of the Association of American Railroads (AAR) (1991).

With regard to the status of AE monitoring as a recognized method in pressure vessel codes, the technique has not achieved this status. The testing of new vessels is adequately covered by existing NDT techniques. Where AE has found a niche is: in the testing of new FRP vessels, where conventional NDT methods are less effective; as a complement to hydrostatic testing; and in the operational monitoring of critical vessels. Since AE is a global inspection method, it appears a strong contender to satisfy any code requirements which may be developed for the inspection of pipework.

19.14.7 AE monitoring procedures

The effective application of AE monitoring requires adherence to a properly formulated procedure. A widely used procedure is MONPAC, developed in and licensed

by Monsanto (1990). The procedure specifies the material and equipment covered, the maximum background noise, and the maximum sensor spacing.

The results obtained in the procedure are allocated to one of five grades, from A indicating minor source/no action, to E indicating intense source/immediate action. An account of the use of MONPAC is given by Cole (1990).

19.14.8 AE monitoring applications: FRP vessels

AE monitoring was applied early to the testing of new metal pressure vessels, but at first with limited success. It was found, however, that AE monitoring was of particular value in the testing and monitoring of FRP pressure vessels.

The use of AE for the testing and monitoring of FRP vessels has been described by Fowler and Scarpellini (1980) and Fowler (1987, 1988), who give an account of its development in one company. Initially the failure rate of FRP vessels, both new and in service, was unacceptable, some of the failures being total ruptures. Many of the conventional NDT techniques are not, however, applicable to FRP. It was therefore attractive to use AE, provided it could be made to work. In fact some problems which occur with the use of the technique on metal vessels, such as background noise, are less severe with FRP. The method proved successful to the extent that there is no record of any significant FRP defect escaping AE testing, and that it became possible to prevent catastrophic failures of FRP vessels. The technique has been adopted within the FRP industry in the USA.

Some relevant standards and codes are given Section 19.14.6.

19.14.9 AE monitoring applications: metal equipment

Despite initial difficulties, AE monitoring of metal equipment has been developed and now constitutes the main area of use. The applications of AE to metal equipment are principally for the monitoring of pressure vessels during hydrostatic pressure testing and of operating pressure vessels, particularly during the transients that occur during start-up and shut-down.

AE monitoring is also used in the testing of certain equipment such as large field-erected storage tanks and vessels in certain special materials such as titanium.

Since it is defect changes which AE monitoring detects, continuous monitoring is less common, but is practised in some instances. In some cases vessels are fitted with permanent equipment for AE monitoring.

The use of AE monitoring during the hydrostatic testing of pressure vessels has been described by McFarland (1970). Adam (1982) has given an account of its use on ammonia storage spheres. Its application to large, refrigerated storage tanks for liquid ammonia, which are difficult to inspect internally, is described by Prasek (1988). Parry (1980) has given an account of its use to investigate potential problems on ammonia converters, including stress corrosion cracking and fretting of shrunk-on bands.

Some applications of AE monitoring to process equipment have been described by Cole (1983). These include a jacketed reactor, a reactor train, a multi-wall high pressure vessel and storage tanks, as well as FRP vessels. For the jacketed reactor, the technique was able to detect defects in the inaccessible space between the shell and the jacket (the 20 minute period following admission of steam to the jacket giving strong acoustic emissions) and associate with thermal stress and corrosion. The reactor train exemplifies early detection of stress corrosion cracking. The multi-layer reactor is an illustration of an equipment that is difficult to inspect by conventional means. The application to storage tanks exploits the technique's ability to give good volumetric coverage.

The application of AE monitoring to propagating fatigue cracks in node joints and crane pedestals on offshore structures is described by L.M. Rogers (1983). Of particular value is the ability of the technique to give global coverage of all welded joints, including those which are otherwise inaccessible.

An application of continuous AE monitoring is that on the blast furnace stove domes at Redcar, described by Cole (1983). Other applications are described in the IChemE *AE Monitoring Guide.*

19.14.10. AE monitoring applications: leaks

High pressure and high velocity leaks give characteristic noise, as does pump cavitation, and the detection of these is another application of AE monitoring. The use of this method to detect tube failures in heat exchangers and boilers has been described by Ghia *et al.* (1983).

19.14.11 IChemE *AE Monitoring Guide*

The IChemE *AE Monitoring Guide* deals with the technique under the following headings: (1) scope, (2) role in structural integrity assessment, (3) applicability to process vessels and pipework, (4) practical requirements, (5) specific examples and (6) practical experience, as given by a user survey. It includes appendices on (1) AE basics, (2) AE test and report specifications, (3) standards and codes, (4) survey returns, (5, 6) questionnaires and (7) bibliography.

The *Guide* emphasizes the importance of defining the purpose for which AE monitoring is to be conducted and gives a flow diagram for the development of the monitoring strategy. The work should be undertaken only if both the plant and the technique are suitable, the level of background noise is not excessive and the exercise is economic.

Under practical requirements the *Guide* deals with the definition of the responsibilities of the operator and the AE contractor, the establishment of the feasibility of AE testing, the experience and qualifications of the contractor, the essential information on the containment, and the test specification, covered in Appendix 1.

The practical applications described cover a liquefied petroleum gas (LPG) storage sphere, an ammonia storage sphere, an ethylene storage bullet, a refrigerated ammonia storage tank and storage tank floor; a nitric acid column, a stainless steel column and an insulated carbon steel and stainless steel columns; a Hastelloy B reactor; a boiler drum; a deaerator; glass reinforced plastic storage tanks for sulphuric acid and hypochlorite; pipework; a crane; and bearings.

Detailed results are given from the user survey, the sections of which cover the number of tests done by the participant companies, the types of test done, the types of structure tested, the materials of construction of these structures, the perceptions of success and the future

intentions. It contains in Appendix 4 single-sheet summaries of individual applications.

The survey indicates that the majority of applications are to metal structures and use commercial packages, principally MONPAC. The main use is for in-service testing of pressure storage vessels and other vessels and storage tanks. More experienced users also conduct pre-service tests.

The *Guide* gives recommendations on the use of AE monitoring.

19.15 Plant Monitoring: Specific Equipment

As the foregoing account indicates, monitoring techniques can be applied to a wide range of plant equipment.

For defects in rotating equipment prime techniques are performance monitoring and vibration monitoring. Another important method is debris analysis.

For static equipment such as tanks, vessels, columns and pipework, widespread use is made of ultrasonics. Such NDT methods are increasingly being complemented by AE monitoring. Corrosion monitoring is another technique that is widely applied, to static plant particularly.

19.16 Pipeline Inspection and Monitoring

19.16.1 Pipeline inspection

Pipelines present a rather different inspection problem from that posed by regular process plant in that they are outside the factory fence, are very long, are usually buried, and are normally required to operate without shut-down.

Traditional methods of inspection include liaison with local farms through whose land the pipeline passes, walking the pipeline and aerial survey of the pipeline. In some cases bar holes may be sunk near the pipeline to take gas detectors. Use may be made of a search gas or radioactive tracer.

Inspections may also be made of the cathodic protection of the pipeline such as checking on coupons of the material and on the pH of the electrolyte in contact with the protected surface.

19.16.2 Inspection vehicles

The alternative to these conventional, and rather limited, methods is the use of an inspection vehicle, or 'intelligent pig'. This device is now routinely used by British Gas for the inspection of its pipeline grid. An account has been given by Braithwaite (1985). The company operates some 17 000 km of high pressure natural gas transmission pipeline in Britain. A typical line interval for inspection is about 80 km.

The inspection specification for the pig required that it should detect, locate and size defects and distinguish defects from other features with a low incidence of spurious indications. Three types of defect were of interest. One is geometric damage, which includes ovality, dents and wrinkles. Another is metal loss due to corrosion or impact. The third is crack-like defects such as plate rolling laminations, stress corrosion cracks and fatigue cracks. The avoidance of spurious indications is of some importance, because frequent spurious indications leading to the excavation of the pipeline would rapidly cause a loss of credibility.

The engineering specification required that it be capable of passing through the line without sudden changes of speed and without jamming in the line.

The pig is designed to operate in pipelines containing gaseous or liquid hydrocarbons. The pig contains three principal systems: the NDT equipment, the electronics and the power pack. There are three NDT systems: one surveys the geometry of the pipe, another detects metal loss, and the third inspects for cracks.

The quantity of data generated by the inspection equipment is very large. An area of $1\,cm^2$ is significant in defect terms and a typical line section of 80 km has an area of some $3 \times 10^9\,cm^2$. It is not practical to store all the data generated and a computer is included to perform on-board data handling.

Braithwaite also describes the selection of the maximum inspection intervals, the field operations and the reporting and rectification procedures.

19.16.3 Pipeline leak monitoring

There are a number of methods available of monitoring for the detection of leaks in pipelines. An account is given by Ellul (1989).

One approach is the use of acoustic monitoring. When a leak occurs, the sudden pressure drop creates a rarefaction wave which propagates away from the leak point at the speed of sound. This wave can be detected by acoustic monitoring.

Acoustic monitoring gives information on the existence and location of a leak, but little on its size. In ideal conditions it can detect very small leaks, but it is less effective against a background of noise from compressors and valves.

An alternative approach is to monitor the behaviour of the pipeline using some form of model. One technique is to determine a line volume balance model over some fixed period. This involves calculating the difference between the inflow and outflow, or net inflow. Different balance intervals are appropriate for different purposes. For a typical pipeline, a short-term balance over 1–2 hours is suitable for relatively rapid detection of the leak, whilst a long-term balance over 3–6 hours gives greater accuracy. Detection of a leak as small as 0.5% of throughput may be achieved.

Use may also be made of a more sophisticated model incorporating values of the pressure, temperature, flow and density at various points in the pipeline. The operation of the line is monitored by comparing the measured and the model values. The occurrence of a leak should cause excursions of some of these parameters outside their control limits. Criteria can be devised to flag the existence of a leak.

19.17 Notation

Section 19.7

c	corrosion allowance
f_a	nominal design strength at test temperature
f_t	nominal time-independent design strength (see text)
p	design pressure
p_t	test pressure

t nominal thickness of section under consideration

Section 19.8

L leak rate ($Pa.m^3/s$)
P pressure (Pa)
t time (s)
V volume of vessel (m^3)

For alternative units see text

Section 19.10

Equations 19.10.1 and 19.10.2

L fraction of gas leaking
p_i suction pressure
p_o discharge pressure
T_i inlet temperature (before addition of bypass gas)
T_o discharge temperature
T_s suction temperature
ΔT_H correction for Joule–Thomson effect
μ constant, approximately equal to ratio of gas specific heats

Equation 19.10.3

A jet nozzle exhaust area
G_a compressor air pumping capacity
N compressor speed
P_d compressor discharge pressure
T_d compressor discharge temperature
T_i turbine inlet temperature
W_f fuel flow
Δ normalized increment of variable
η compressor efficiency

20 Plant Operation

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Accidents on process plants arise as often from deficiencies of operations as from those of design. It is difficult, therefore, to overstress the importance of plant operations in safety and loss prevention.

Accounts of plant operation include *Process Plant Design and Operation* (D. Scott and Crawley, 1992) and those by E. Edwards and Lees (1973) and London (1982). Some reference to plant operation is also made in many of the Chemical Industries Association (CIA) codes and guidelines and the Health and Safety Executive (HSE) guidelines mentioned in Chapter 11. Selected references on plant operation are given in Table 20.1.

Many aspects of operation are dealt with in other chapters. In particular, these include: plant management (Chapter 6); hazard identification (Chapter 8); pressure systems (Chapter 12); process control (Chapter 13); human factors (Chapter 14); fire protection (Chapter 16); plant inspection (Chapter 19); plant maintenance and modification (Chapter 21); emergency planning (Chapter 24); personal safety (Chapter 25); and information feedback (Chapter 27).

Table 20.1 *Selected references on plant operation*

NRC (Appendix 28 *Nuclear Power Plant Operation, Operational Safety Reliability Program, Operation*); American Oil Company (n.d./1–10); MCA (SG-2); J.R. Howard (1959); Steinhoff (1959, 1973); Anon. (1961a); Gimbel (1965a); W.H. Richardson (1966); Holroyd (1967); Badger (1968); Lofthouse (1969); O.M. Allen and Hanna (1971); E. Edwards and Lees (1973, 1974); IP (1973 Eur. MCSP Pt 1); Kauber (1973); API (1975 RP 50); Neal (1976); Anon. (1977 LPB 14, p. 2); Blair (1977); *Chemical Engineering* Staff (1980); IBC (1981/21); London (1982); Roodman (1982); H.W. Martin (1983); Kolff and Mertens (1984); Burgoyne (1985c); Tayler (1985d); Rausch (1986); Cloke (1988); Kister (1981a,b, 1990); G.K. Chen (1987); AGA (1988/55); EPA (1988/1); Trask (1990); McConnell (1992); D. Scott and Crawley (1992); R.E. Sanders (1993b)
Site register: RoSPA (IS/77)
Communications: Bach (1968); Anon. (1976 LPB 10, p. 4)
In-plant chemicals labelling: Kmetz (1990)
Production control, material balance, quality control: Tingey (1962); Hearfield (1975); Oakland (1981)

Start-up and shut-down, turnarounds
American Oil Company (n.d./4); Anon. (1960f); Ballmer (1964); Bonnel and Burns (1964); Hayes and Melaven (1964); Lieber and Herndon (1965, 1973); Loen (1966, 1973); Nobles (1967); Luus (1971); FPA (1972/16); Barnett (1973); H.S. Moody (1974); Kister (1979, 1981a); API (1982 *Refinery Inspection Guide* Ch. 18); Bauman (1982); H.V. Bell (1982); Rattan and Pathak (1985); Feuless and Madhaven (1988); Butler, Nayar and Wheeler (1993); Nimmo (1993)

Boilers, burners, furnaces, flares (see also *Table 12.3*)
S.R. Green (1952); Bluhm (1961, 1964b); P.W. Taylor (1964); FMEC (1967); OIA (1971 Bull. 501); Charlton (1973); HSE (1975 TDN 25); NFPA (1990 NFPA 86)

Storage, terminals
H.T. Fuller and Bristline (1964); J.R. Hughes (1970); PITB (1973/5); Hearfield (1975); MCA (1975 TC-8, TC-27, TC-28, TC-29); Anon. (1976 LPB 9, p. 1); Chlorine Institute (1979 Pmphlt 9, 66, 1982 Pmphlt 5, 1984 Pmphlt 78, 1986 Pmphlt 1); API (1982/5); NFPA (1990 NFPA 307)

Operating activities
Purging: AGA (1954, 1975); Constance (1980); Anon. (1989 LPB 90, p. 1); Levinson (1989); Schneider (1993)
Sampling: MCA (SG-16); Ducommun (1964a,b); ICI/RoSPA (1970 IS/74); Gitzlaff and Batton (1979); Lovelace (1979); Chlorine Institute (1984 Pmphlt 77); Anon. (1989 LPB 88, p. 1); Anon. (1990 LPB 92, p. 27); Anon. (1992 LPB 106, p. 19)
Draining: Klaassen (1980b); Anon. (1991k)
Additives, catalysts: W.S. Wood (1963); Brand and Burgess (1973)

Operating procedures, instructions, manuals (see Table 14.2)

Leaks and spillages
ICI/RoSPA (1970 IS/74); Bess (1972); Home Office (1972/9); MCA (1973/22); AIChE (1974/99, 1988/100); Kletz (1975b, 1981g, 1982i); Anon. (1987 LPB 74, p. 1)

Winter conditions
IRI (n.d./1); Buehler (1967); House (1967); API (1983/8)

Security
FPA (CFSD SEC series, 1972/19); NRC (Appendix 28 *Security*); IRI (n.d./4); Hamilton (1967); NFPA (1971/7); Payne (1971); IMechE (1972/5); Oliver and Wilson (1972); K.G. Wright (1972); C. Ward (1973); G. Green and Faber (1974); Flood (1976); Atallah (1977); W. Price (1978); D.L. Berger (1979); Spranza (1981, 1982, 1991, 1992); Bailey (1983); Lobel (1985); Anon. (1987 LPB 77, p. 17); Pitt (1987)

The present chapter deals with some important aspects of operation which are not treated elsewhere. These are:

(1) operating discipline;
(2) operating procedures;
(3) emergency procedures;
(4) handover and permit systems;
(5) operator training;
(6) plant patrols;
(7) modifications to the process;
(8) operation and maintenance;
(9) start-up and shut-down;
(10) start-up of refinery units;
(11) shut-down of refinery units;
(12) operation of fired heaters;
(13) operation of driers;
(14) operation of storage;
(15) operational activities and hazards;
(16) sampling;

(17) trip systems;
(18) identification measures:
(19) exposure of personnel;
(20) security.

Before considering these detailed aspects, however, it is emphasized again that the safe operation of hazardous plants requires in particular competent and experienced managers and formal, well considered and fully understood systems of work. The aspects of operation mentioned are now discussed.

20.1 Operating Discipline

The safe operation of a process plant requires adherence to a strict operating discipline. This discipline needs to be formulated, along with the safety precautions, during design and then enforced in operation. An account of operating discipline is given by Trask (1990).

The impetus for the development of operating disciplines in the author's company came in the 1960s from the perceived need to ensure that the technology was uniformly applied in all the company's plants, both in the UK and overseas, and in the 1970s from the need to ensure that human technical skills were maintained in the face of increasing automation.

The steps involved in developing the operating discipline are: (1) to identify the important operating parameters, specify operating limits on these parameters, and arrange for them to be measured, controlled and monitored, using both trend records and alarms; (2) to ensure mass and energy balances; and (3) to develop and document operating procedures, safety precautions and remedial actions.

20.1.1 Operating envelope

The design of the plant specifies the conditions at which it is to operate. In some cases, such as operation at different throughputs, it may specify several sets of conditions. There is, however, a degree of latitude in operation, and some divergence from the nominal design conditions is acceptable. In fact, since the design embodies inaccuracies of various kinds, it is inevitable.

It is necessary, therefore, to define the envelope of conditions within which variations are allowed but across which excursions are not permitted. In the first instance, this envelope is defined by the designer in terms of constraints related to the pressure envelope, such as vessel design pressure and temperature limits, and also to the process conditions such as flow limits related to static electricity or temperature limits related to freezing or hydrate formation. The envelope may subsequently be modified to some degree on the initiative of the plant management, but in consultation with the design function. At any given time, however, the operational envelope should be clearly defined and strictly enforced.

20.2 Operating Procedures and Instructions

Fundamental to the safe operation of plant is the development of suitable operating procedures. The procedures are normally formulated during the plant design and are modified as necessary during the plant commissioning and operation.

20.2.1 Regulatory requirements

In the UK the provision of operating procedures is a regulatory requirement. The Health and Safety at Work etc. Act (HSWA) 1974 requires that there be safe systems of work. A requirement for written operating procedures, or operating instructions, is given in numerous codes issued by the HSE and the industry.

In the USA the Occupational Safety and Health Administration (OSHA) draft standard 29 CFR: Part 1910 on process safety management (OSHA, 1990b) states:

(1) The employer shall develop and implement written operating procedures that provide clear instructions for safely conducting activities involved in each process consistent with the process safety information and shall address at least the following:
(i) Steps for each operating phase:
  (A) Initial start-up;
  (B) Normal operation;
  (C) Temporary operations as the need arises;
  (D) Emergency operations, including emergency shutdowns, and who may initiate these procedures;
  (E) Normal shutdown; and
  (F) Start-up following a turnaround, or after an emergency shutdown.
(ii) Operating limits:
  (A) Consequences of deviation;
  (B) Steps required to correct and/or avoid deviation; and
  (C) Safety systems and their functions;
(iii) Safety and health considerations.
  (A) Properties of, and hazards presented by, the chemicals used in the process;
  (B) Precautions necessary to prevent exposure, including administrative controls, engineering controls, and personal protective equipment;
  (C) Control measures to be taken if physical contact or airborne exposure occurs;
  (D) Safety procedures for opening process equipment (such as pipe line breaking);
  (E) Quality control of raw materials and control of hazardous chemical inventory levels; and
  (F) Any special or unique hazards.
(2) A copy of the operating procedures shall be readily accessible to employees who work in or maintain a process.
(3) The operating procedures shall be reviewed as often as necessary to assure that they reflect current operating practice, including changes that result from changes in process chemicals, technology and equipment; and changes to facilities.

20.2.2 Operating procedures

Accounts of the generation of operating procedures and instructions have been given by R. King (1990) and I.S. Sutton (1992).

In designing a plant, the designer necessarily has in mind the way in which it is to be operated. It is desirable that this design intent be explicitly documented, otherwise it has to be inferred from the equipment provided. In the case of batch and other sequential processes the designer normally defines the operations required to execute the sequence.

Practice in the formulation of operating procedures varies. The lead is normally taken by the plant manager. In the case of a new plant the commissioning manager is often the prospective plant manager, and will therefore undertake the task.

Operating procedures may be developed using a team of experienced people who examine successively the procedures necessary for testing and pre-start-up activities, normal start-up, normal shut-down, emergency shut-down, etc.

The information required in order to formulate procedures includes: the order in which operations should be carried out; the valve states and valve changes associated with each operation; the time required to perform the operation; and the operations which have to be completed before another operation can be initiated.

For a new plant an initial set of operating procedures is devised, but these are likely to be modified as the result of experience during the commissioning. Likewise, procedures for an existing plant will undergo changes based on operating experience, as well as changes due to process or plant modifications.

The extent to which process operators are involved in the formulation of operating procedures varies. Some operating procedures are modelled on the practice of the 'best' operator. Operators also devise short cuts. These should be examined, and accepted or rejected, as appropriate, with reasons given.

A formal method of analysing the operator's task is available in task analysis, which is described in Chapter 14.

It is the task of management in formulating operating procedures to clear up muddled thinking, to identify incorrect assumptions, to resolve differences and to eliminate inconsistencies. The ultimate responsibility for the operating procedures rests with the plant manager.

20.2.3 SRDA *Operating Procedures Guide*

A systematic approach to the development of operating procedures is given in *Developing Best Operating Procedures* (Bardsley and Jenkins, 1991 SRD SRDA-R1) (the SRDA *Operating Procedures Guide*).

The SRDA *Guide* distinguishes between two basic types of documentation to support operator performance: (1) manuals and (2) job aids. Essentially a manual is a resource, which is a store of information to which managers, engineers and trainers may refer. The information contained in it, however, is usually not in a form best adapted for direct use by the operator. What he requires for immediate use is a job aid.

Operator support documentation may take the form of (1) procedures, (2) checklists or (3) decision aids. The simplest form of procedure is a set of actions which are performed in sequence with a minimal feedback requirement. More complex procedures involve actions which are dependent on a lapse of time and/or the state of the process, or which involve sets of actions other than a straightforward sequence. The typical checklist is an *aide memoire* used to check the state of items on the plant, notably valves, prior to undertaking some operation such as start-up. Decision aids, in the form of decision trees, or flowcharts or algorithms, guide the operator through the decision pathways. There are also other types of decision aid, used particularly for fault diagnosis, such as functional diagrams. In addition to these specific forms, documents often contain explanations.

The *Guide* poses six basic questions to be asked concerning the operator's use of a support document. The writer needs to ask how the operator decides when to use the document, how he locates the document itself and how he locates the required help within it. Furthermore, the writer must ask whether the document provides the information sought in a form such that appropriate action is selected, whether it indicates the circumstances in which an alternative course of action is required and whether it states how the action is to be controlled. Finally, the writer should check that the document has been successful by means such as monitoring of feedback.

In addressing the question of operator support documentation, the first step is to establish that there really is need for it. One general justification is compliance with regulatory requirements or company policy. Another justification is the nature of the task.

On this the *Guide* both gives some general pointers and also outlines some specific techniques. With regard to the former, some task characteristics which may indicate the need for job aids are that: it is critical; it is difficult, e.g. fault diagnosis; it is performed infrequently, e.g. an emergency procedure; and/or it is long and involves memory load. If a job aid is to be provided, there must be time for it to be located and used.

It needs to be borne in mind that a job aid may not prove as effective as expected. Some reasons for this are that it remains unused, that it is seen as taking the skill from the task and that it may restrict the choices available to a skilled person.

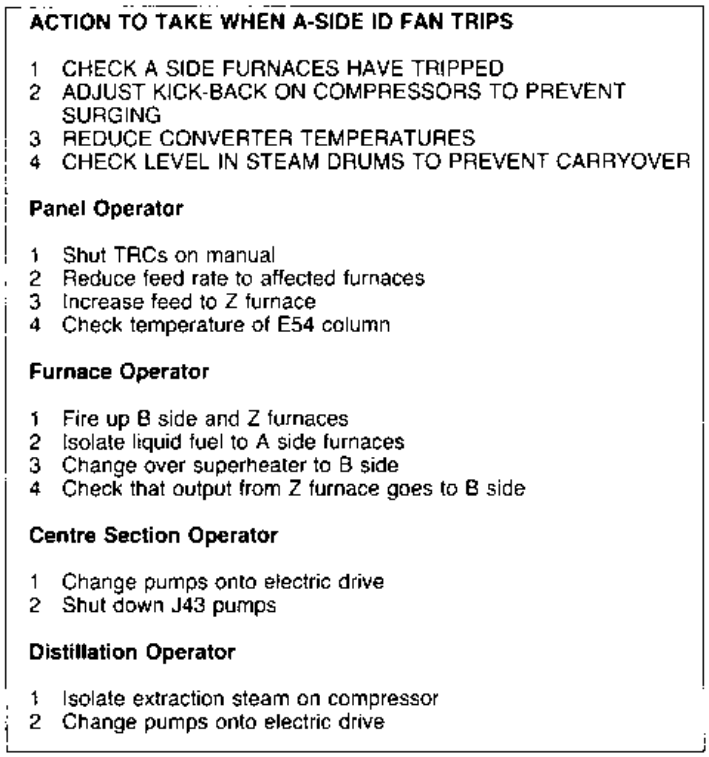
The specific techniques referred to are those of task analysis and human reliability analysis.

The *Guide* describes the process of designing and implementing an operating support document in terms of the following stages: (1) the definition of the purpose and scope and the selection of a format (manual or job aid), (2) the establishment of collaboration with sources of information, (3) the establishment of information content, (4) the prototyping, (5) the preparation of a draft, (6) a review of the draft both for technical content and usability, (7) implementation and (8) maintenance.

An account is given of hierarchical task analysis and of human reliability analysis, both of which have been described in Chapter 14. In respect of the latter, the two techniques considered are SHERPA and CADA.

The writing of an operating support document which can be understood requires careful attention both to the written text and to the alternatives to such text. Aspects of the written text treated in the *Guide* are: the use of a comprehensive vocabulary, supported if necessary by a glossary, and of conventional terms as opposed to jargon; the use of the active rather than the passive tense; care with the use of negatives; retention of the definite and indefinite articles; the use of short sentences; the presentation of instructions as a sequence; and an indication of any applicable pre-conditions. The *Guide* gives detailed guidance on character style, punctuation and layout.

The *Guide* also describes the use of tables and figures. Tables provide a good format for stating the courses of action to be taken in different situations. The types of table given are the condition–action table and the



ACTION TO TAKE WHEN A-SIDE ID FAN TRIPS

1 CHECK A SIDE FURNACES HAVE TRIPPED
2 ADJUST KICK-BACK ON COMPRESSORS TO PREVENT SURGING
3 REDUCE CONVERTER TEMPERATURES
4 CHECK LEVEL IN STEAM DRUMS TO PREVENT CARRYOVER

Panel Operator

1 Shut TRCs on manual
2 Reduce feed rate to affected furnaces
3 Increase feed to Z furnace
4 Check temperature of E54 column

Furnace Operator

1 Fire up B side and Z furnaces
2 Isolate liquid fuel to A side furnaces
3 Change over superheater to B side
4 Check that output from Z furnace goes to B side

Centre Section Operator

1 Change pumps onto electric drive
2 Shut down J43 pumps

Distillation Operator

1 Isolate extraction steam on compressor
2 Change pumps onto electric drive

Figure 20.1 *Format of operating instructions: extract from a plant instruction showing the action to be taken by an operating team of one supervisor and four operators when the induced draught (ID) fan providing air to a row of furnaces (known as A side) stops (Kletz, 1991e) (Courtesy of the Institution of Chemical Engineers)*

decision table, both akin to a truth table, and the look-up table. The types of figure described are decision aids in the form of flowcharts, and various kinds of equipment diagrams, including photographs. Equipment diagrams include: drawings, or sketches, of single equipments or ensembles, which are useful for identifying and locating components; line diagrams showing the main items of equipment and the connections between them; and functional flow diagrams giving the functional as opposed to the physical structure of the system.

Guidance is also given on document organization and layout. A hierarchical organization is recommended and aids to moving around the document are described. The need for consistency is emphasized.

Finally, the *Guide* discusses the tools available for the production of the document such as word processors, desk top publishing packages, object oriented drawing packages, and so on.

20.2.4 Operating instructions

Accounts of the writing of operating instructions from the practitioner's viewpoint are given by Kletz (1991e) and I.S. Sutton (1992).

Operating instructions are commonly collected in an operating manual. The writing of the operating manual tends not to receive the attention and resources which it merits. It is often something of a cinderella task.

As a result, the manual is frequently an unattractive document. Typically it contains a mixture of different types of information. Often the individual sections contain indigestible text; the pages are badly typed and poorly photocopied; and the organization of the manual does little to assist the operator in finding his way around it.

Operating instructions should be written so that they are clear to the user rather than so as to absolve the writer of responsibility. The attempt to do the latter is a prime cause of unclear instructions.

A set of instructions which illustrates the above principles has been given by Kletz, as shown in Figure 20.1. Further examples are given by Sutton.

This latter author describes a method of writing the operating instructions, and of creating the operating manual. Basic requirements for the operating instructions are that they should be complete, up-to-date, properly indexed and easy to use.

The operating manual is organized in the format of a tree which is developed from the top down. It which starts with broad categories of procedure such as start-up, normal operation, normal shut-down, etc., and is developed until it reaches, at the bottom level, the sets of specific operating procedures, or modules. It may be

noted that this layout conforms closely to the tree structure used in task analysis.

A distinction is made between information, rules, procedures and checklists. Information is provided for reference, but selectively. Rules are stated, although these are likely to be of more interest to managers and supervisors than to operators. Checklists are given as appropriate.

Instructions are given for each procedure. The procedure may be based on a generic procedure, such as that for pump start-up, but with specific modifications for the operation in question. The level of the instructions should be such as to allow an experienced operator to run the plant with minimal reference to the supervisor. Each instruction should have an imperative verb in the active tense. Warnings, cautions and notes are inserted in the text of the procedure, as appropriate; a warning should precede the procedure.

As described by Sutton, a module may be referenced in any part of the manual and by any writer, but only by its title; reference should not be made to the content of the module. This discipline, which has much in common with that followed for computer program subroutines, facilitates the up-dating of the manual by allowing a single module to be replaced at any time.

The manual is more readable by basing it on graphics rather than text so that the text supports the graphics rather than vice versa. Modules are written in a two-page format, which is what the user actually sees at a given time.

The manual should define clearly the authorization for particular actions.

Commonly the manual contains a section on trouble-shooting. This activity is quite different from that of following a procedure for normal operation. Such a procedure is a closed activity and the instructions for it are intended to be followed without deviation. Trouble-shooting, by contrast, is open-ended and creative. The procedures for it are not definitive and do no more than offer guidance.

The creation of the operating manual involves, first, the definition of the manual structure, then the collection of the information and, finally, the writing of the modules. Sutton estimates that his method may involve an effort which is an order of magnitude greater than the conventional approach. A further account of the creation and contents of the operating manual is given by R. King (1990), with a detailed discussion of suitable contents.

Commonly the operating manual is a hard-copy document. It should be available on the plant. Some personnel may be given a personal copy. Authority to make modifications to the manual should be clearly defined. The manual should be kept up to date, including personal copies where issued.

The advent of computer aids such as word processing and graphics packages opens up an alternative approach in which the master version of the operating manual is kept in the computer with various options for hard copy.

In addition to the treatment given by these three authors the following comments may be made. Regard should be had to the intended users of the operating intructions. These include (1) novice operators, (2) operators whose experience has been on other plants but who are being trained for the plant in question and (3) operators experienced on that plant. The organization of the operating manual into successively more detailed levels goes some way towards meeting their different needs. An experienced operator may require operating instructions mainly for safety critical operations or operations performed only rarely.

The simplest operating instruction is a linear sequence of actions. There is a limit to the degree to which an operating instruction may be extended to include decision trees, branches and loops. Generally these are avoided if possible, except for diagnosis. On the other hand, it is common to include general advice about and/or specific instructions for recovery from potential problem situations.

Practice with regard to use of graphics appears to vary. As stated, Sutton's approach is that the text is there to support the graphics. At the other end of the spectrum operating instructions are written which make minimal use of graphics.

Operators are typically provided with operating instruction sheets/checklists which may well be reproductions of sheets in the operating manual and which they can take out onto the plant. It may also be appropriate to provide other aids such as a list of alarms and trips.

The writing of the operating instructions is a significant task. Some principal sources of information are the quantities flowsheet, the engineering line diagram, the design manual and vendors' manuals. The contractors may provide very little and vendor information may become available only late in the day. The situation is eased if an operating manual is available from a previous plant.

The first task faced by the person charged with producing operating instructions tends actually to be the provision of instructions for commissioning. This can be as large a task as the creation of the instructions for normal operation. Commissioning activities for which instructions may need to be provided include plant water testing, control loop testing, load cell testing and checks on vessel fill times, completeness of vessel emptying, and heating and cooling rates. The instructions should also cover checks to ensure that before an equipment is brought into use each of its instruments is operational.

Many operations involve the reading of instruments. The instructions need to specify the readings at which action must be taken. A considerable part of the effort required to write the instructions may have to be devoted to specifying these readings and the writer may have to search through a number of documents. In addition, water testing requires some readings to be specified also for water as the fluid.

In devising operating instructions regard should be had to the practicality of the individual actions and sequence of actions required. It is not desirable, for example, to create a sequence of actions in which one has to be performed at the top of a tower, the next back down at ground level and the next up at the tower top again. Another area where thought it necessary is the response to alarms and the settings on alarms. For example, the implications of and the response times available for a particular fractional fill may be different from one vessel to another.

If the plant is a computer-controlled batch plant the number of operator interventions may be quite small and may involve relatively little decision-making. In this case

the operating instructions proper are likely to be a mix of computer sequences with occasional manual operations such as additions and instructions on recovery from problems.

The operators will require training in the operation of the plant based on the operating instructions. It is necessary, therefore, to provide a training manual. This may draw on the operations manual. Typically it contains an operating instruction section together with other material such as a training plan, workbook exercises, an assessment plan and performance criteria. The need for a training manual may be regarded as a principal justification for the creation of the operating manual. Training in operating procedures is discussed in Chapter 14 and is mentioned in many other chapters.

20.3 Emergency Procedures

A set of operating procedures of particular importance are the emergency procedures. It is generally recognized that it is not possible to provide detailed procedures for all possible emergency scenarios. In the *Guide to Safe Practice in the Use and Handling of Hydrogen Fluoride* (CIA, 1978) the following two-pronged approach is recommended:

> Firstly, careful consideration should be given to what major emergencies can be reasonably foreseen, and the detailed procedure for tackling these (few) serious situations should be dealt with specifically both by training sessions and special instructions.
>
> Secondly, since it is impossible to cover all eventualities by instructions which will be effectively remembered or found for reference during an emergency, it is advisable to give a series of general instructions, amply backed by training, which will provide guidance for the correct action in those emergency or potential emergency situations which have not been dealt with by specific cases. Such aspects as equipment isolation, the recognition of hazardous conditions, and communications are fundamental matters which can be treated in this way.

Emergency procedures are commonly treated in codes under the following headings: (1) leak detection and characterization; (2) raising the alarm and associated actions; (3) isolation of leaks; (4) handling of leaks and spillages; (5) action against fire; (6) emergency equipment; and (7) special features of particular chemicals.

These topics are considered at this point, except that raising the alarm and associated actions are treated in Chapter 24 and the treatment of action against fire is limited, the main account being given in Chapter 16.

20.3.1 Emergency equipment

Emergency equipment commonly listed in codes includes (1) protective clothing, (2) breathing apparatus, (3) emergency tool kits, and (4) fire fighting equipment.

20.3.2 Leaks and spillages

Leaks and spillages are a relatively common occurrence on process plants and it is necessary to have procedures for dealing with them. Discussions of leaks and spillages have already been given in Chapters 10, 15, 16 and 18 in relation to plant layout, dispersion, fire and toxic release. It is appropriate here, however, to review some of the more general aspects of the problem from the operational point of view.

Plant management should formulate procedures for dealing with leaks and spillages. The range of actions required varies with the nature and size of the leak. In all cases personnel handling the leaks should wear any necessary protective clothing and breathing apparatus.

A small leak may often be stopped relatively easily. If the leak is more serious, other measures are required. The ICI *LFG Code* (ICI/RoSPA 1970 IS/74) lists these for liquefied flammable gases. If it is practical to do so, the leak should be isolated. This is not always possible with manually operated valves which may be enveloped in the gas cloud. Remotely operated isolation valves may be used if installed. Instructions should take account of possible difficulties in effecting isolation. Other measures to reduce leakage include depressurizing and blowdown.

Personnel involved in controlling the situation should avoid entering the vapour cloud. The leak should be approached only from upwind. Other personnel should not be allowed in the area. There should be some method of warning and evacuating them, and also of sealing off the area.

Measures should be taken as appropriate to disperse or contain the leakage. This aspect is discussed in Chapters 15 and 16.

The area to which a flammable vapour cloud is likely to spread should be cleared of sources of ignition, which include not only activities such as hot work but also traffic. It may be necessary to close roads and railways which the vapour could reach.

The emergency services should be alerted as appropriate.

After the incident is over, any record required by the reporting system should be made.

20.3.3 Leaks and spillages: detection and characterization

For large releases detection of a leak and characterization of the resultant cloud are important. These are discussed in the CCPS *Guidelines for Vapor Release Mitigation* (1988/3).

For detection the first line of defence is gas detectors. The *Guidelines* discuss the detectors available and their positioning. Accounts of detectors for flammable and toxic gases are given in Chapters 16 and 18, respectively.

On most plants there are personnel who may detect the presence of the gas. Detection by humans is discussed in *The Perception of Odors* (Eugen, 1982) and data on odour thresholds are available in texts such as *Compilation of Odor and Taste Threshold Value Data* (Fazzalari, 1978). Selected data are given in the *Guidelines*. Appendix 11 contains a further discussion of odours.

If a leak occurs which gives rise to a large vapour cloud, it assists in handling the emergency if personnel are able to estimate the size and movement of the cloud. Their ability to do so depends on its visibility. A small number of substances yield, at a sufficiently high concentration, a vapour cloud which is visible by virtue of its colour. Principal examples are chlorine and bromine, which give a greenish yellow and a reddish orange cloud, respectively.

A more common form of visible cloud is that caused by fog formation. Liquefied flammable gases and other

liquefied gases such as ammonia, hydrogen chloride and hydrogen fluoride may give rise to fog, depending on the conditions of release and the atmospheric humidity. The *Guidelines* devote an appendix to fog correlations and give the following relation for the concentration at the interface between the regions where fog is and is not generated

$$C = k \ln(1/\psi) \quad [20.3.1]$$

with

$$k = \frac{1.75 \times 10^6}{H_s^2} \quad [20.3.2]$$

where C is the interface concentration (ppm), H_s is the heat of solution (cal/gmol), ψ is the fractional humidity (% relative humidity/100) and k is a constant.

20.3.4 Leaks and spillages: water and foam

One method of dealing with a liquid spillage is the application of foam. Regular foam is mainly water and its use will often actually increase the rate of vaporization of the spilled liquid, thus making the situation worse. On the other hand, there are legitimate uses of foam. The use of foam on liquid spillages is discussed in Chapter 15. Some limited comments are given below.

If the chemical is completely miscible with water, water may be applied to dilute it. However, the number of industrial chemicals which pose a significant hazard and which are water miscible is limited.

20.3.5 Leaks and spillages: particular chemicals

The response to a leak or spillage emergency depends also upon the specific characteristics of the chemical released.

For hydrocarbons the main hazard is that of fire or explosion, and also that of injury by freezing due to contact with cold liquefied gas. The best way of dealing with an unignited leak of hydrocarbon is to shut it off by isolation. A spillage of liquid hydrocarbon should be contained to the extent possible. This is principally a matter of plant layout and the operational measures which can be taken are fairly limited.

The CIA codes and guidelines give some guidance on handling leaks and spillages of other substances. Mention is made here of just one or two of these to illustrate the principles involved.

An acrylonitrile spillage should be contained with sand or earth and covered with a 150 mm layer of mechanical foam and an emulsifying agent or absorbent material. Aqueous solutions may be treated with calcium or sodium hypochlorite in appropriate proportions. Where these treatments are not readily available, surface spillages may be diluted with large quantities of water.

A spillage of ethylene oxide may be handled by diluting it with a quantity of water sufficient to render it non-flammable. This may be done using water sprays or, where available, water monitors. It may be noted, however, that in discussing the disposal of the contents of a storage tank the guidelines state that it is not usually practical to dilute liquid ethylene oxide to the point of non-flammablity and that liquid which has not been rendered non-flammmable needs to be treated as a flammable liquid.

For a vinyl chloride spillage the preferred method of control is the use of high expansion mechanical foam. For this not to aggravate the situation the pool needs to be not still spreading but contained and at least 2 in. deep.

20.3.6 Action against fire

A large proportion of plant fires are due to hydrocarbons. If the fire consists of an ignited leak burning as a jet flame on the plant, the usual practice is to let it burn. It is generally not desirable to seek to extinguish the flame on such a leak, since this risks creating a vapour cloud, which might then explode. The other main form of hydrocarbon fire is a pool fire. The fighting of hydrocarbon fires is discussed in Chapter 16.

There is a limited amount of guidance in the CIA codes and guidelines on action against fire of other substances. The guidance given for pool fires of vinyl chloride (CIA, 1978 PA15) illustrates some of the principles. For a large pool fire, foam can be effective in limiting vaporization and thus in controlling the fire. There is an option to seek to extinguish the fire by using a larger quantity of foam but, unless there are pressing reasons for doing otherwise, it is preferable to let the fire burn out under controlled conditions.

Vinyl chloride also illustrates the problem of toxic combustion products, the products in this case being hydrogen chloride and carbon monoxide. Use may be made of water sprays to disperse and absorb some of the hydrogen chloride. But in any event persons downwind should be evacuated.

20.3.7 Case history

A case history has been described which illustrates the value of good emergency procedures (Anon., 1991 LPB 98 p. 25). In the course of a stress relieving operation on a 50 mm pipe on a chlorine storage module, a 0.5 m section was burned away by an iron–chlorine fire. The leak was picked up by the gas detectors, the gas alarms operated and the operator went to investigate. He called on the lead operator to sound the chlorine alarm, donned a breathing apparatus set and went and closed the appropriate valves. The site emergency teams arrived and within 3 minutes set up water curtains, but these were not needed as the leak had already been isolated and the cloud was dispersing.

20.4 Handover and Permit Systems

20.4.1 Handover systems

Most large process plants operate round the clock on a shift system. It is essential that information on the state of the plant be communicated by the outgoing shift to the incoming shift. A formal handover system is necessary to ensure this.

The lack of such a system was held to have been a cause of the Piper Alpha disaster. As described in Appendix 19, the operating crew attempted to start up a pump which was actually under maintenance and thus initiated the leak. The lead maintenance hand told the Inquiry that there were no written procedures for handover and no specification of the information to be communicated at handover. Thus maintenance work was not always covered in the operator's log. He stated:

'There were always times when it was a surprise when you found out some things that were going on'. As it happens, the Piper Inquiry also heard evidence that shortly before the disaster a fatal incident had occurred in which there had been inadequate communication of information from the day shift to the night shift.

There should be a formal and detailed procedure for shift handover. It should cover both operating and maintenance personnel. On the operating side these will normally include the lead operator, the control room operator and other operators who are normally out on the plant, and the lead maintenance hand. There should be a formal logbook which is signed by the incoming person responsible for the particular function. Such a system requires that sufficient time be allowed for the handover to take place and for the outgoing shift to brief fully their counterparts on the incoming one.

An aspect of handover which is of particular importance is the status of permits-to-work. Much of the information which needs to be communicated at handover is likely to relate to such permits.

20.4.2 Permit systems

Another important form of communication is the permit-to-work system just mentioned. Permits are raised mainly in connection with maintenance work and discussion is deferred to Chapter 21. Here it is sufficient to note that the actions of handing over a section of plant to maintenance, and receiving it back, are important not only for maintenance but also for the operating function.

20.5 Operator Training

The process operator runs the plant and deals with the faults which arise on it. He has many training needs which must be met if he is to do the job properly. An account of the principles underlying the training of process operators has been given in Chapter 14. This chapter also discusses some of the specific topics in the area of process operation on which the operator requires training. Safety training of operators is considered in Chapter 28. Other references to operator training are given throughout the text.

As regards the content of operator training, consideration needs to be given not just to the operating procedures and safety training, but also to other topics where the operator has some responsibility. These include, for example, plant maintenance and modification and plant security.

The training of process operators should not be a once-and-for-all exercise, but should involve updating as appropriate. There may also be special additional training such as that associated with the commissioning of a new plant.

20.6 Plant Patrols

One of the principal functions of operators on process plants is the detection of faults. The detection of faults by the process operator in the control room has already been discussed. Other faults, particularly leaks, are detected by operators during routine patrols.

In one study of the detection of nearly 400 abnormal occurrences, analysis showed that some 40% were detected by routine patrols and another 5% by people who were in the plant area.

An investigation of pipework failures by Bellamy, Geyer and Astley (1989) found the following pattern of detection:

	No. of incidents	*Proportion of incidents* (%)
Alarm	12	26
Automatic detection	4	8.5
Human	27	57
Delayed	4	8.5
Total	47	100.0

Routine patrolling is therefore important and specific arrangements need to be taken to ensure that it is carried out. In particular, steps may be taken to ensure that certain vulnerable features are regularly passed by an operator. Thus in design certain instruments may be located at points which cause the operator to pass by such features, whilst in operation instructions may be issued for the taking of regular readings from such instruments.

20.7 Modifications to the Process

A process rarely operates for long without undergoing some modification. There are almost always changes in raw materials, in the operating conditions, such as flows, pressures and temperatures, concentrations, or in other aspects. The Flixborough disaster has drawn attention to the potential hazards of modifications to the plant. But modifications made to the process are also potentially hazardous.

As it happens, Flixborough provides an illustration of a process modification also. The reactors were provided with agitators, but at the time when the explosion occurred the agitator in No. 4 Reactor was not in use. The absence of agitation is a crucial point in the hypothesis advanced by R. King (1975c, 1977, 1990) that there was a sudden evolution of water vapour in that reactor.

There is clearly little point in paying meticulous attention to ensuring close control of plant modifications so that the pressure system retains its capability to handle the design conditions for the operating variables, if there is no check on changes made to these parameters. A system is required, therefore, for the management of change in the process as well as in the plant. A system for the control of both process and plant modifications is described in Chapter 21.

20.8 Operation and Maintenance

Maintenance and modification work may present hazards both to the plant and to the workers involved. It is important, therefore, for the plant manager to give full consideration to the implications of such work being carried out on his plant and for him to take appropriate precautions. As a minimum these precautions should be the operation of a suitable permit-to-work, as described in

Chapter 21, but in addition some operations require extra measures.

The types of precaution which may be required are illustrated by those described by Hahn (1975) for hot tapping. This is a potentially hazardous operation involving drilling a hole into, and fitting a branch on, a pipe while it is still on line; the technique is described more fully in Chapter 21. The aspects requiring consideration include (1) pipeline fluid conditions, (2) elimination of leaks, (3) local hazards, (4) emergency isolation, (5) warning system, (6) access and escape routes, (7) fire and rescue services, (8) welders' protective clothing, (9) welding supervision and (10) operations supervision.

The plant manager should check the pipeline fluid conditions, such as flow, pressure and temperature, under normal operation, should agree with the welding manager the conditions to be held during the hot tapping operation and should take steps to ensure that these are maintained. The drains in the area of the welding operation should be sealed off and a review made of sources of flammable or obnoxious materials such as leaking joints or lutes. Any local hazards, including those not connected with the welding operation, should be considered and the personnel involved should be fully briefed about these hazards. Arrangements should be made to isolate the pipeline and affected areas in the event of an emergency. A warning system should be set up to inform plant personnel and emergency services if an emergency occurs. Access should be checked so that emergency services can reach the tapping point and the plant, and the areas sealed off to other traffic if necessary. A check should also be made on escape routes, which at night may need additional illumination. A rescue man from the works fire service should stand by during the operation with a radio link to the fire station to summon the fire rescue services in an emergency. He should be prepared for fire fighting and should have the necessary equipment. A plant fireman should also stand by. A check should be made that the welders have the appropriate protective clothing. The work should be supervised by personnel from both the welding and the plant functions. If possible, the plant manager should be present.

The arrangements described indicate that some maintenance or modification work requires the rather close involvement of the operations side.

20.9 Start-up and Shut-down

As take-off and landing are more hazardous operations for an aircraft, so on a process plant the hazard is greater during start-up and shut-down. General principles of plant start-up and shut-down are discussed by D. Scott and Crawley (1992). The procedures for the start-up, operation and shut-down of particular types of plant are considered in the following sections.

Most accounts of the operation of process plants distinguish the following modes:

(1) normal start-up;
(2) normal operation;
(3) normal shut-down;
(4) emergency shut-down.

Shut-down is not always total. Sometimes there is a partial shut-down to a condition of 'hot standby'. This avoids the need to go through the full sequence of shut-down and start-up operations, and allows operation to be resumed more quickly.

There are, however, further relevant distinctions. Leaving aside the initial start-up when the plant is commissioned, there are variations in start-up depending on the condition of the plant prior to start-up. Some distinctions are:

(1) normal shut-down condition;
(2) hot standby condition;
(3) emergency shut-down condition;
(4) major scheduled shut-down, or turnaround, condition;
(5) prolonged shut-down, or mothballing, condition.

The condition of the plant following emergency shut-down depends on the cause of the shut-down, and hence this category actually includes a whole set of different pre-start-up conditions.

The start-up considered here is not the initial commissioning, which is dealt with in Chapter 19, but the resumption of operation after a shut-down.

The actual procedures for start-up and shut-down depend on the process, and vary somewhat. Start-up of a plant with a low temperature section, for example, has special features.

20.9.1 Normal start-up

Start-up requires that the plant be taken through a predetermined sequence of stages. It is important that this sequence be planned so that it is safe and avoids damage to the plant and so that it is flexible enough to handle difficulties which may arise. The conceptual and detailed design of the start-up sequence is discussed in Chapter 11. The personnel involved in the start-up should understand the reasons for the sequence chosen and should adhere to it.

The extent to which detailed procedures can be formulated for start-up depends on the condition prior to start-up. For start-up following a major scheduled shut-down it may not be practical to provide fully comprehensive instructions and it may be necessary to rely instead on the use of checklists for equipment and activities. On the other hand, for start-up from hot standby or a short shut-down it may be possible to provide relatively complete procedures.

Start-up is an operation which needs to be properly planned so that all the resources are available when required. This applies particularly to personnel, e.g. instrument fitters, and to utilities, e.g. inert gas.

Start-up should be preceded by a series of pre-start-up checks. These should be governed by a formal system. The plant is first checked to ensure that it is mechanically complete, that there are no missing items such as valves, pipes or instruments, that the status of vent, drain and sample points is correct and that slip plates have not been erroneously left in pipework. A check is then made to ensure that the instruments are working. The availability of the utilities is confirmed. The hand valves are then checked to ensure that the status of each is correct.

In many cases the plant is linked through flows of products and by-products to other plants and the start-up

needs to be co-ordinated with the operation of these interlinked plants. Similar considerations apply to the utilities.

Many plants generate services such as fuel gas, steam or electricity which they reuse and recover heat through complex heat exchange arrangements. Features of this sort add considerably to the complications of start-up.

The start-up period is one when serious damage can be inflicted on plant equipment. Thus mention has already been made of the danger of using up a large proportion of the creep life during commissioning. Similar damage can be inflicted in regular start-ups.

Start-up is a time when there is a much higher than average risk of getting unwanted materials such as air or water into the plant. It is necessary to pay particular attention to these hazards.

Instruments are of particular importance during start-up, but unfortunately are likely to be less accurate or reliable than during normal operation. This should be borne in mind if an instrument failure could give rise to a hazardous condition.

It is an essential requirement, therefore, that there be a formal but practical system to control start-ups, that there be proper documentation and that the personnel be fully trained in the procedures.

20.9.2 Normal operation

The normal operation of the plant is discussed in Chapter 13 and is not considered in detail in this section, but there are several points that may be restated.

The plant management should ensure that the objectives of, and constraints on, the operation of the plant are clearly defined and well understood by the process operators.

There should be a full understanding of the relative roles of the operator and the trip system in the face of a developing abnormal condition. In essence, it is the function of the operator to try to prevent this condition developing to the point where a parameter goes outside its permitted envelope and that of the trip system to shut down if such an excursion is imminent.

It is desirable that there be holding states, or fall-back positions, short of full shut-down, to which the operator can move the plant while a problem is sorted out.

In any event, management must make it clear beyond doubt that any conflict between production and safety is to be resolved in favour of the latter.

20.9.3 Normal shut-down

Normal shut-down starts from the condition of normal operation and its preceding condition is therefore relatively well defined. This makes it practical to formulate shut-down procedures more fully than for some of the start-up situations mentioned.

Many of the features of start-up mentioned earlier, such as the effect on other plants and on utilities, apply *mutatis mutandis* to shut-down.

20.9.4 Emergency shut-down

Emergency shut-down may be effected by an automatic protective system or by the operator. In the first case the operator's function is to forestall the activation of the automatic system by averting the threatened parameter excursion, whilst in the second he has the additional function of performing the shut-down if it becomes necessary.

In some systems an intermediate case occurs, where the automatic system shuts down part of the plant but it is left to the operator to shut down other parts. This is the case, for example, on some oil production platforms, where the main oil line may be shut down automatically but the gas lines to and from the platform, which are linked to other platforms, are shut down manually, thus allowing a degree of co-ordination with other platforms which would be affected.

The emergency shut-down procedure is generally designed so that the conditions which should trigger it are unambiguously identified and the actions to be taken are clearly defined. A typical shut-down condition is the imminent excursion of a parameter. Typical shut-down actions are shutoff of heat input and depressurization of vessels.

For emergency shut-down by the operator, emergency shut-down procedures should be provided, in the form of a general emergency shut-down procedure. There may be some variability in this procedure depending on the event forcing the shut-down, but an excessive number of variations should be avoided.

These emergency shut-down procedures are to be distinguished from the procedures required to deal with escapes from the plant, which are generally referred to as emergency procedures.

Emergency shut-down is discussed further in Chapters 13 and 14.

20.9.5 Prolonged shut-down

If shut-down is prolonged, precautions should be taken to prevent deterioration of the plant. Typical examples are inspection of equipment to check for external corrosion and 'turning over' of pumps to avoid 'brinelling'. Prolonged shut-down, and start-up from this condition, is discussed further in Chapter 10.

20.9.6 Restart after discovery of a defect

If it is necessary to shut the plant down on account of a fault, the cause and implications of the fault should be established and any necessary measures taken before the plant is started up again. This situation should be covered by a procedure which details the steps to be taken after such a fault is discovered and before the plant is restarted.

At Flixborough it was found that No. 5 Reactor had developed a crack 6 ft long, but the plant was put back on stream without a thorough examination of the other reactors, an omission which is criticized in the *Flixborough Report*.

20.10 Start-up of Refinery Units

Accounts of the start-up and shut-down of refinery units are given in *Safe Ups and Downs* (American Oil Company, Amoco/4) and by Hayes and Melaven (1964).

Some principal hazards are:

(1) mixing of air and hydrocarbons;
(2) contacting of hot oil and water;
(3) water shots and water freezing;
(4) over- and underpressuring of equipment;
(5) thermal and mechanical shock to equipment;

(6) corrosive and poisonous fluids;
(7) pyrophoric iron sulphide.

The last item is a hazard mainly during shut-down, but the other hazards occur during both start-up and shut-down. Fired heaters present particular hazards and are dealt with in Section 20.12.

Start-up should include the following phases:

(1) preparatory activity;
(2) removal of air;
(3) leak testing;
(4) disposal of purge material;
(5) removal of water;
(6) bringing on stream.

The plant should be inspected to check that it is ready for start-up. The auxiliary systems such as the utilities, instruments and gland oil systems should be activated. Shut-down blinds should be removed and running blinds installed.

There are various hazards associated with the activation of the steam system, including water hammer, overpressuring, and thermal and mechanical shock. Steam should be introduced into the unit gently, with vents and drains open. When the unit is up to temperature, the vents and drains should be closed and the steam traps commissioned. Measures should be taken to avoid collections of condensate which may give rise to water hammer or may freeze.

The activation of the water system presents the hazards of introducing water where it is not wanted and of its freezing. Water connections used only for washing down during shut-down should be blinded off.

There should be a formal procedure with proper documentation for the installation and removal of blinds, so as to ensure that all blinds installed for shut-down purposes are removed and all blinds required for running are installed.

Air should be removed by purging with a suitable material. This is commonly done using water or steam. Use is also made of inert gases such as nitrogen, carbon dioxide or gas from an inert gas generator.

Steam is an effective material for purging. Besides removing air, it vaporizes water, melts ice and reveals blockages in vents and drains. The purging should be done with high-point vents and low-point drains open, but with instrument connections closed except on pressure gauges. The steam should generally be introduced at the bottom of the unit, not only because it is lighter than air and tends to rise but also because this gives a refluxing and cleaning action which is not otherwise obtained.

Purging may also be carried out by filling with water. High-point vents should be opened and the unit filled until the water flows out of the top. Water purging may be done by filling several equipments simultaneously. This method is suitable, however, only if the water will do no damage to process features, e.g. catalysts, and if the equipment is capable of supporting the weight of water.

Another method of purging is the use of inert gas. The purging should be done with vents and drains open. The pressure should be kept positive, but low so as not to waste gas.

If an inert gas generator is used, the quality of the gas should be monitored. It is necessary for the oxygen content of the gas to be kept well below the target value for the atmosphere in the unit in order to avoid using excessive quantities of the gas.

Closed systems, such as flare and blowdown systems into which relief valves discharge, should also be purged with inert gas. This may require special purge connections.

With steam or inert gas, purging should be continued until analysis shows that the oxygen content is below the desired level. This is typically 0.5% v/v or less.

The vent and drain points at which analytical tests are to be made should be specified and records kept of the tests.

Vacuum equipment may be freed of air by evacuating and refilling with inert gas, this cycle being repeated two or three times.

The equipment should then be raised to a suitable pressure to allow testing for leaks. The testing is carried out by closing the vents and drains after purging and admitting more steam, water or inert gas until the required pressure is reached. All joints and connections should then be inspected for leakage. Leak testing is considered in more detail in Chapter 19.

The positive pressure should be maintained in the equipment after the test. With steam or water a few high-point vents may be opened and a small flow maintained. Condensate should be drawn off periodically from low-point drains. With inert gas, vents and drains should be kept closed.

Vacuum equipment should be given a leak test under pressure, as just described, followed by a vacuum test.

It is then necessary, except for vacuum equipment, to remove the purge materials. This is normally done using fuel gas, which is an essentially hydrocarbon material, is readily available and can be returned to the fuel gas system.

If steam is the purge material, there should be a gradual and simultaneous opening of the fuel gas valve and closing of the steam valve. Drains should be cleared of condensate and both vents and drains closed when the fuel gas flows out.

It is important to allow sufficient fuel gas in the unit to maintain a positive pressure and avoid either allowing air in if the vents are open or underpressuring the unit if the vents are closed.

If the purge material is water, the vents should be closed, the fuel gas admitted at the high point, the drains opened, and the water gradually displaced. Drains should be closed when the fuel gas comes out.

If inert gas purging is used, the fuel gas should be allowed to flow in and mix with the inert gas.

In all cases the fuel gas flow should be maintained until the required pressure is reached. If this is the normal fuel gas line pressure, the unit may be left connected to the line, while if it is some lower pressure, the unit should be shut off or left connected but under pressure control.

With vacuum equipment the purge gas is removed by evacuation.

Residual water should now be removed before hot oil is introduced. This is done by circulating oil which is initially cold (10–40°C) and is then heated to warm (40–80°C) or hot (80–175°C or above). Generally, the oil used is that normally charged to the unit, but suitable low pour point gas oil can be utilized.

While the cold oil is circulating, water should be drained from the system. Since a water–oil emulsion may form, the circulation should be interrupted every 30–40 minutes to let the emulsion break and the water settle so that it can be drained off.

When water is no longer draining, the oil temperature should be raised to warm. This may release some more water by melting ice and breaking emulsions. This water also should be drained away.

If the unit normally operates below the boiling point of water, it is not usually necessary to raise the oil temperature further, but if it operates at higher temperatures, then the oil temperature should be raised to hot.

Usually at this stage the oil flow is changed from circulatory to once-through, the oil being pumped to specified receivers.

Units which operate at higher temperatures often have their own fired heaters and these can be started up and used to heat the oil.

The instrumentation should be brought into service as far as is possible during these operations.

Additional flushing of sections of the unit such as reflux lines and drums and blowdown lines should also be carried out using warm oil. There should be frequent draining of water to prevent violent contact with hot oil. The exact procedures depend on the type of unit.

Finally, the unit should be brought on stream by making the specified staged adjustments to the main parameters, such as flow, pressure and temperature, until the normal operating conditions are reached. This is generally straightforward, but certain hazards may occur. The equipment may be subjected to overpressure or thermal or mechanical shock. Common causes are too rapid changes in operating parameters or a lack of appreciation of the temperature relations between different parts of the system. Water and air may again find their way into the plant from various sources.

20.11 Shut-down of Refinery Units

The same sources also describe the shut-down of refinery units. Shut-down should include the following phases:

(1) cooling and depressurizing;
(2) pumping out;
(3) removal of residual hydrocarbons;
(4) removal of corrosive or toxic materials;
(5) removal of water;
(6) blinding activities;
(7) removal of pyrophoric iron sulphide.

The heat input to the unit should be stopped and fired heaters shut down. The feed flow should be reduced and then cut off. Excess pressure should be relieved by releasing the hydrocarbon gases to the gas collecting system.

If cooling might cause underpressure, inert gas should be introduced to maintain the pressure close to atmospheric.

Vacuum units should be cooled, the vacuum-producing equipment shut off and the vacuum broken by introducing inert gas.

When the unit is cooled and depressurized, the materials should be pumped out to specified receivers.

Care should be taken that during pumping out centrifugal pumps are not allowed to lose suction completely, since even a short period of running dry can do serious damage. Reciprocating pumps are less susceptible.

The oil pumped out should be cooled so that it is below its flashpoint and is sufficiently cold not to cause trouble if it contacts water in the lines.

The pressure in the unit should be maintained during pumping out by admitting inert gas so that underpressure and air inleak are avoided.

Residual hydrocarbons should then be removed by purging with steam, water, or water followed by steam. Details of shut-down purging methods are given by Hayes and Melaven (1964).

After purging, air should be allowed into the unit. The inflow of air should be sufficient to prevent underpressure.

Residual corrosive or toxic materials which may be present should likewise be removed. Essentially similar purge materials and methods may be used. A further discussion of equipment purging and cleaning for maintenance is given in Chapter 21.

Water left in the unit from normal operations or from purging should be removed to prevent damage during the downtime and start-up. Freezing of water in the equipment can do serious damage and should be avoided. The water should be completely drained from the unit and blocked drains identified and cleared.

The installation of shut-down blinds and the removal of running blinds should then be carried out under the control of a proper procedure with appropriate documentation, as already described. The methods of isolation and line breaking are described in Chapter 21.

If there is a possibility that pyrophoric iron sulphide might be present, men should stand by ready to spray the sulphide when the equipment is opened up. The fluid used may be water or a suitable light oil. The latter wets more thoroughly and evaporates less rapidly, and may be preferable unless it constitutes a further fire hazard. Complete mechanical removal of the sulphide should then be carried out.

20.12 Operation of Fired Heaters

The operation of a rather different item of plant is illustrated by that of fired heaters. Some of the hazards of fired heaters and some features of their design relevant to safety are discussed in Chapter 12. Here consideration is given to the safe start-up and operation of such units.

Safe operation of fired heaters is dealt with in *Safe Furnace Firing* (American Oil Company, Amoco/3), *Handbook of Industrial Loss Prevention* (FMEC, 1967) and the CCPS *Engineering Design Guidelines* (1993/13) and in the codes and other publications cited in Chapter 12.

20.12.1 Burner start-up

The essential features of the safe start-up of burners have been described above, but some of these may be re-emphasized in relation to operation.

Every effort should be made to prevent the leakage of fuel into the firing space. Shut-off valves should be checked for leak tightness. Double block and bleed

valves should be operated as intended, with the bleed valve open when the block valves are closed.

It should be appreciated that it may not take long for fuel sufficient to create a flammable atmosphere to pass into the firing space. With oil firing the quantity flowing in the few seconds between the flame extinction and shut-off valve may be enough, while with gas firing a flammable mixture may form by leakage through a shut-off valve during the few minutes which it takes to remove a slip plate. Partly for this reason slip plates are not considered a good means of isolation for gaseous fuel. Leakage flows of gas through shut-off valves are often in the range 1–10 l/min.

The air flow should be established and the firing space purged by opening the dampers and starting the fans.

The atmosphere in the firing space should be tested before ignition is attempted. Delay between this test and the ignition should be avoided. If time does elapse, a repeat test should be made.

If a separate device such as a pilot burner is used to effect ignition, this should be lit before the fuel to the burner is turned on. A check should be made that the pilot light is established. The check should be on the flame itself rather than on some quantity from which the presence of the flame might be inferred.

If the main flame goes out, the proper start-up procedure, including purging and testing of the firing space, should be carried out. Short cuts such as simply attempting to relight the burner should not be taken.

The presence of a flame should be monitored by a flame failure device. The device should 'see' the flame to be monitored and not other flames such as the pilot light.

If there are multiple burners, it should be borne in mind that fuel may leak through from burners which are shut off so that a flammable mixture is formed and is then ignited by an operating burner. In some circumstances, it may be appropriate to avoid this by firing with all the burners.

The flame is normally extinguished by shutting off the fuel and injecting snuffing steam.

The possibility of interactions between furnaces linked by common headers should be borne in mind.

20.12.2 Tube failures

Overheating of furnace tubes can result in rapid or delayed failure. Rapid failure can occur if the flow of feed through the tubes is too low or is lost altogether, or if there is direct flame impingement on the tubes. Failure can also result from less intense overheating over long periods. It is very easy to cause a drastic reduction in the creep life of tubes by maloperation.

Typically a furnace tube has a creep life of 10 years at 500°C. Then its creep life will be reduced approximately as follows by operation at higher temperatures:

Temperature (°C)	*Creep life*
506	6 years
550	3 months
635	20 hours

The reduction in creep life is *pro rata*. Thus, for example, the creep life for a tube with the characteristics just given will be used up by operation for 5 years at 500°C and $1\frac{1}{2}$ h months at 550°C.

The measurement of the furnace tube temperature is difficult, but temperature measuring devices are available for this duty. It is now normal practice to measure the tube temperature. The measurements may be used to generate alarms to warn the process operator and/or to initiate trips which shut the furnace down. A trip system may be effective against gross overheating, but is less appropriate to prevent overheating which is not so severe, but which can nevertheless cause a serious reduction in creep life.

It is essential, therefore, for the process operator to understand the penalties of overheating and, in particular, those arising from the relatively small increases of tube temperature which he may otherwise regard as insignificant.

20.13 Operation of Driers

An item of equipment which has much in common with a fired heater but is rather more complex is a drier. An account of the start-up, operation and shut-down of a drier is given in *Prevention of Fires and Explosions in Driers* (the IChemE *Drier Guide*) (Abbott, 1990).

There are a number of different types of drier. Abbott gives first a general account of the operation of a drier, which, broadly, is applicable to any type, and then considers the variations applicable to particular types of drier. The account given here is based on this general account and assumes that inerting is used.

20.13.1 Pre-start-up checks

Before the drier is started up, checks should be made on the mechanical condition of the plant, its internal state, its instrumentation and the control settings. There should be no leaks of fuel or lubricating oil and the air filter should be clean. Explosion vents should be intact and clear to operate. The plant should be free of spillages and deposits and of maintenance equipment. The instrument should be operational, as should explosion suppression devices. The damper settings should be correct. It should also be checked whether there has been any modification to the plant or the material to be dried.

20.13.2 Normal start-up

Essentially, the operation of a drier involves steering a course between overheating or underdrying the product. The product temperature must not be allowed to rise to a point where a runaway reaction can occur and deposits in the drier must not reach their self-ignition temperature. On the other hand, the product must not be underdried which, besides giving off-specification material, can cause blockage in the discharge system and caking in conveying and storage.

It is also necessary to ensure that the exhaust gas temperature remains above its dewpoint in the dust recovery equipment. The exhaust gas temperature is controlled by manipulating (1) the heat input, (2) the feed flow, and/or (3) the evaporative load. The heat

input is the variable principally used, but the response may be slow due to large time lags.

The plant should be started up by starting the product discharge valves and conveyors and the fans. On an indirectly heated drier the heating medium should then be admitted. Assuming, as stated, that the system is operated under inert gas, it should be purged until the outlet oxygen concentration has fallen to the operating value. Assuming also that the heater is fired by gas or oil, it should be started up using a safe fired heater start-up procedure. Once the exhaust gas temperature has reached its operating value, the feed of wet material should be started.

The drier is then gradually brought up to full load, within the constraints mentioned. This is generally the stage of the process that is most difficult to control.

20.13.3 Normal operation

In normal operation the same control objectives apply, i.e. to avoid overheating or underdrying the product, and the same means of control are available. The operation of the heater should be closely monitored. The product should be checked for specks of burned, charred or discoloured material, signs of a smouldering or burning deposit in the drier.

20.13.4 Normal shut-down

The same control objectives apply for normal shut-down. Again the process passes through a critical stage as conditions pass through a transient.

The shut-down is initiated by shutting off the feed. Then the heater is shut off. Purging with inert gas is continued until all the product material has left the drier. The inert gas is then purged from the drier with air. The fan, discharge valves and conveyors can then be switched off.

The inside of the drier should be inspected under a permit-to-work system. Potential hazards include a low oxygen content and smouldering material.

20.13.5 Emergency shut-down

The appropriate procedure for emergency shut-down depends on the condition causing the emergency. This may be a material blockage, an equipment failure, or a fire or explosion.

For either of the first two events, the objective should be to prevent overheating of the product. Methods available are to shut off the heat input, to get the material out of the drier and to maintain the evaporative load. One way of effecting the latter is the use of a water spray.

The emergency procedures for dealing with a fire or explosion are given in the *Drier Guide*.

20.14 Operation of Storage

A large number of incidents occur associated with the bursting or collapse of atmospheric storage tanks due to maloperation.

An atmospheric storage tank is typically designed to withstand an internal pressure of 8 in. WG (20 mbar) or a vacuum of $2\frac{1}{2}$ h in. WG (6 mbar). These are very low pressures, which it is easy to exceed unless there is careful operation.

If the pressure inside the tank is not kept within these limits, the failure of the roof or of the side walls may occur. Two principal modes of failure are overstressing of the roof due to excessive internal pressure and instability of the side walls due to excessive vacuum.

Generally a roof fails under internal pressure either at the seams between the roof and the side walls or along the diametral seams in the roof itself. The failure typically has a cod's mouth appearance. Large tanks are particularly vulnerable.

For internal pressure the shear stress σ_s in the seam between the roof and the wall is proportional to the pressure p and the diameter d and inversely proportional to the thickness of the tank wall t:

$$\sigma_s \propto pd/t \qquad [20.14.1]$$

The bending stress σ_b in the roof itself is proportional to the internal pressure and the square of the diameter and inversely proportional to the square of the thickness:

$$\sigma_b \propto p(d/t)^2 \qquad [20.14.2]$$

The side walls are designed to withstand the maximum head of liquid which can occur in the tank. The internal pressure is thus relatively less important in this case. But, again, the hoop stress in the side wall σ_h due to the internal pressure is proportional to the pressure and the diameter and inversely proportional to the thickness:

$$\sigma_h \propto pd/t \qquad [20.14.3]$$

The vulnerability of large storage tanks to overpressure may be illustrated by considering the relative stresses in the roof and side walls of (1) a baked bean tin and (2) a 1000 m^3 fixed roof storage tank. It is assumed that the baked bean tin has a diameter of 7.5 cm and a thickness of 0.25 mm, and that the storage tank has a diameter of 12 m and a thickness of 5 mm. Then the ratios of the stresses in the tin and in the storage tank are as follows:

	Stress in storage tank / *Stress in baked bean tin*
Side wall, σ_h	8
Roof, σ_b	64

Similarly, for vacuum the stresses are much greater in large tanks.

The effect of vacuum on the side walls of a storage tank is to induce instability. The analysis of tank instability is complex, but some understanding may be obtained by considering the effects of slight distortions in the shape of the tank. These effects may be summarized by saying that for internal pressure small changes in shape do not tend to cause the side walls to fail, but for vacuum such changes do tend to cause failure.

This situation may be explained by the following simplified argument (Aird, 1977b). Consider a small element of the wall of the storage tank, as illustrated in Figure 20.2(a), where r is the radius of the tank, t is the thickness of the wall, δ is the width of the element and the angles α and ϕ and the vectors of forces F_1 and F_2 are as shown. Then with an internal pressure p and an external pressure of zero

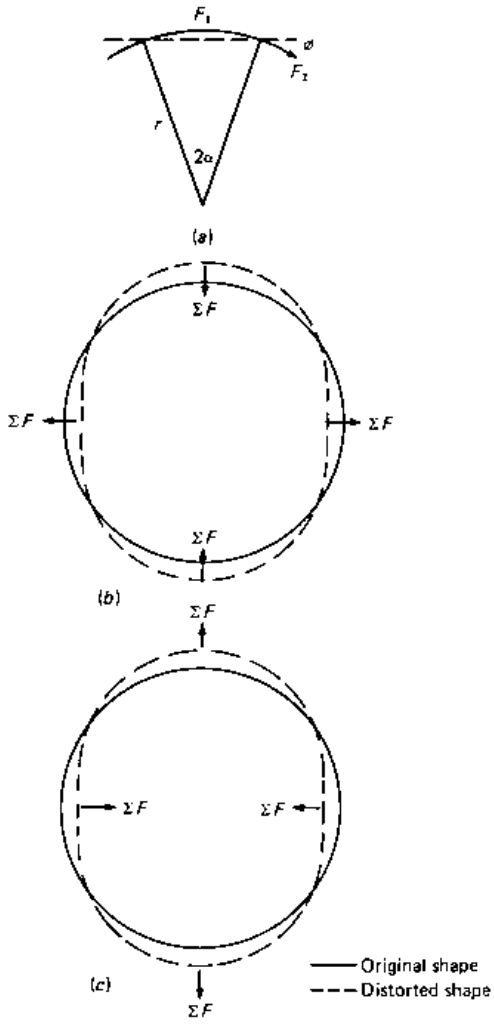


Figure 20.2 *Forces acting on the side wall of an atmospheric storage tank: (a) element of side wall; (b) positive internal pressure – resultant forces tend to correct distortion; (c) negative internal pressure – resultant forces tend to reinforce distortion*

$$F_1 = \int_{-\alpha}^{\alpha} p\delta r \cos\theta \, \mathrm{d}\theta \qquad [20.14.4a]$$

$$= 2p\delta r \sin\alpha \qquad [20.14.4b]$$

$$= 2p\delta r\alpha \qquad \alpha \ll 1 \qquad [20.14.4c]$$

$$F_2 = \sigma_h t\delta \qquad [20.14.5]$$

where σ_h is the hoop stress.

The vector of forces ΣF in the vertical direction in Figure 20.2(a) is thus

$$\Sigma F = F_1 - 2F_2 \sin\phi \qquad [20.14.6a]$$

At equilibrium this vector of forces must be zero

$$\Sigma F = 0 \qquad [20.14.6b]$$

For the case where there is no distortion of the element

$$\phi = \alpha \qquad [20.14.7]$$

Hence from Equations 20.14.4–20.14.7

$$\sigma_h = \frac{pr}{t} \qquad [20.14.8]$$

and

$$F_2 = pr\delta \qquad [20.14.9]$$

Now consider the cases where distortion occurs. For a small inwards distortion

$$\phi < \alpha \qquad [20.14.10]$$

and hence

$$\Sigma F = 2p\delta r(\sin\alpha - \sin\phi) > 0 \qquad [20.14.11]$$

Thus the net resultant force due to distortion tends to move the element outwards and so to return it to its original shape. For outwards distortion

$$\phi > \alpha \qquad [20.14.12]$$

and hence

$$\Sigma F < 0 \qquad [20.14.13]$$

Thus the resultant force due to distortion tends to move the element inwards and so again to return it to its original shape. These effects are shown in Figure 20.2(b).

Conversely, with an internal vacuum the vector of forces in the vertical direction is

$$\Sigma F = -F_1 + 2F_2 \sin\phi \qquad [20.14.14]$$

For inwards distortion relation 20.14.10 applies and hence

$$\Sigma F < 0 \qquad [20.14.15]$$

Thus the resultant force due to distortion tends to move the element inwards and so reinforce the distortion. For outwards distortion relation [20.14.12] applies, and hence

$$\Sigma F > 0 \qquad [20.14.16]$$

Thus the resultant force due to distortion again tends to move the element outwards and so reinforce the distortion. These effects are shown in Figure 20.2(c).

A fuller treatment is given by den Hartog (1952, p. 274).

Atmospheric pressure is maintained in a storage tank by a vent to the atmosphere. The tank may be subjected to pressure or vacuum which it cannot withstand, not only if this vent is blocked, but also if it does not have the capacity to handle the flows required to equalize the pressure.

Some ways in which overpressure can occur include (1) pumping in liquid too fast, (2) an increase in the temperature of the liquid contents, (3) pumping hot liquid into water, and (4) blowing in air, steam or gas.

An increase in the temperature of the liquid in the tank can occur due to pumping in hot liquid or to a high ambient temperature. For many substances a temperature rise of 6 C is enough to give an increase in vapour pressure of 8 in. WG. Pumping hot oil into water raises

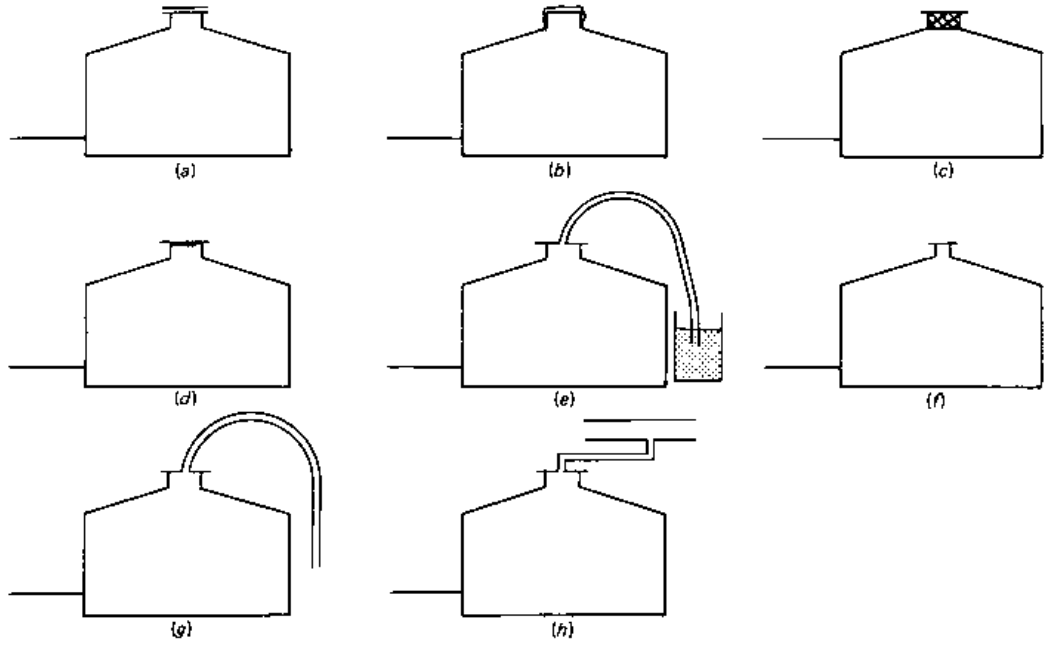


Figure 20.3 *Some vent conditions which can lead to the bursting or collapse of an atmospheric storage tank: (a) vent blanked off; (b) plastic bag over vent; (c) vent choked; (d) flame trap choked; (e) vent connected to water seal; (f) vent too small; (g) flexible tubing connected to vent; (h) vent modified*

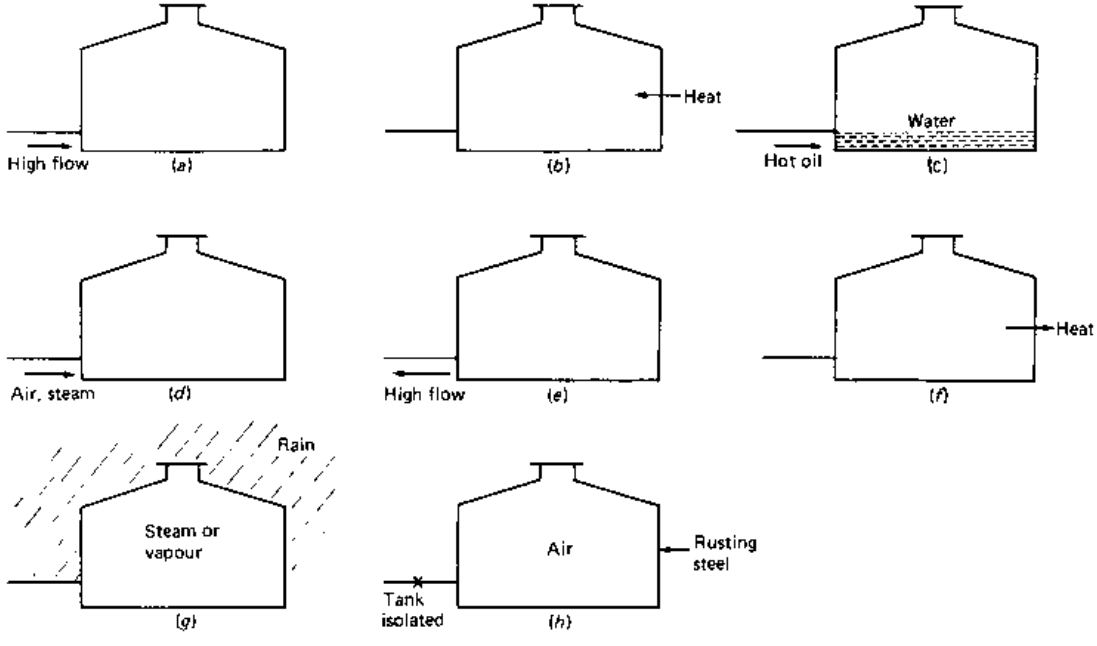


Figure 20.4 *Operations and situations which can lead to the bursting or collapse of an atmospheric storage tank: (a) overpressure – pumping in liquid too fast; (b) overpressure – increase in the temperature of liquid contents; (c) overpressure – pumping hot oil into water; (d) overpressure – blowing in air, steam or gas; (e) vacuum – pumping out liquid too fast; (f) vacuum – decrease in the temperature of liquid contents; (g) vacuum – condensation of steam or vapour; (h) vacuum – depletion of oxygen*

the water temperature and causes it to exert a higher vapour pressure, or even to boil off as steam.

Similarly, ways in which vacuum can occur include (1) pumping out liquid or emptying liquid under gravity too fast, (2) a decrease in the temperature of the liquid contents, and (3) condensation of the steam or vapour contents or a depletion of the gas content.

Condensation of steam or vapour in the tank can occur as a result of a sudden shower of rain.

Vents on tanks are liable to blockage by debris or by polymerization or crystallization of the liquid. The vent normally has a flame arrester, which is particularly liable to blockage. Vents are sometimes blanked off to allow maintenance work to be done.

It is emphasized, however, that it is not necessary for a vent to be blocked for a tank to burst or collapse. All that is required is for the vent capacity to be insufficient to handle the flow required to equalize the pressure.

The systems to which an atmospheric storage tank is likely to be connected mostly are at, or can generate, pressures sufficient to overpressure the tank. This applies to equipment such as transfer pumps and to services such as steam, air or nitrogen.

Some situations which can lead to the bursting or collapse of a storage tank are shown in Figures 20.3 and 20.4. Bursting or collapse may result from a combination of the vent conditions shown in Figures 20.3 and the operations or situations shown in Figure 20.4.

As an illustration of storage tank collapse, consider the following case. Welding had to be done near the roof of a storage tank containing a volatile flammable liquid soluble in water. The tank had an open vent with a flame arrester on it. The maintenance supervisor connected a flexible tube to the flame arrester and immersed the other end of the tube in a drum filled with water. When liquid was run out of the tank a vacuum developed and the tank, designed to withstand $2\frac{1}{2}$ in. WG, collapsed inwards. Moreover, if instead liquid had been run into the tank, overpressure would have developed corresponding to the depth of immersion of the tube and the tank, designed for 8 in. WG internal pressure, would have burst.

Other examples of storage tank collapse are described in Case Histories B44–B48.

20.15 Operational Activities and Hazards

20.15.1 Water hammer

The term 'water hammer' is applied to two somewhat different phenomena, both of which generate forces sufficient to rupture the pipeline.

One kind of water hammer, or hammer blow, results from the sudden closure of a valve in a long pipeline filled with water. The force on the valve is then proportional to the rate of dissipation of the momentum of the fluid. Such water hammer is familiar in domestic water systems, where its effects are usually not serious. On an industrial scale, however, hammer blow can be very destructive. The phenomenon is considered in more detail in Chapter 12.

The other kind of water hammer occurs when a slug of condensate is flung against the pipework by steam. Typical features of a situation giving rise to this effect are as follows. The steam main is not used for some time, but the steam pressure is maintained. Condensate collects at low points. The steam traps and drains which should drain the condensate out are not working. The steam flow is suddenly increased and water hammer occurs. Again the effect can be highly destructive.

Steam mains should be designed to allow condensate to be drained from low points by steam traps and drains. These traps and drains need to be maintained so that they work effectively. It is a help if they are so installed that they can be drilled through under pressure if they get blocked.

It is also essential to exercise care when it is necessary to make large alterations to steam flows, particularly in situations such as start-up. Suitable precautions are checks on condensate accumulation and on the operation of steam traps, and slow operation of the steam valves. It should be appreciated that alteration of the opening of a valve in a steam ring main can have a great effect on the flows in that main.

Both kinds of water hammer, but particularly the first, can occur with fluids other than water.

20.15.2 Slopover

If hot oil is brought into contact with water, there is liable to be a rapid evolution of water vapour and the formation of a large volume of foam. This condition typically occurs when oil with a water layer is heated up or when hot oil is run into a vessel containing water, or oil and water. The effect is similar to that occurring when wet chips are put into boiling fat in a chip pan. It is variously known as 'slopover', 'boilover', 'foamover' and 'puking'.

The effect created when water is vaporized is illustrated by the eruption of the volcano Krakatoa in 1883. A cubic mile of water was vaporized and a cubic mile of rock was thrown into the air. Rock fragments travelled to a height of 14 miles and the sound was heard 3000 miles away.

Incidents involving slopover are quite frequent and can be serious. Slopover is one of the hazards described in *Hazard of Water* (American Oil Company, Amoco/1).

Although it is water which is most commonly involved, a similar phenomenon can occur with a volatile oil. A serious accident which was probably caused by this effect occurred at the Shell refinery at Pernis in 1968 (Fontein, 1968). Hydrocarbons in a slops tank boiled over. A vapour cloud formed, found a source of ignition and exploded violently, causing extensive blast damage and a large fire. Owing to cold weather, it had been necessary during the two previous weeks to heat the oil in the tank. It is believed that the steam coils had become covered in a water-in-oil emulsion which reduced the heat transfer to the supernatant oil, so that the two oil layers were at substantially different temperatures, and that vapour formation at the interface between the oil layers initiated mixing, causing further vapour evolution so that the tank overflowed, the hydrostatic pressure at the bottom of the tank was reduced and violent boil-up occurred. The incident is described in Case History A41.

20.15.3 Water draining

In the storage of liquefied petroleum gas (LPG) small amounts of water usually accumulate in the vessel. This water is commonly removed by the periodic action of an

operator who drains it off manually. If for any reason the operator loses control, a hazardous situation is liable to arise in which the fluid issuing from the drain point is no longer water but LPG.

This hazard was realized in the Feyzin disaster in 1966, described in Case History A38, where an operator found himself unable to shut off the valves at the bottom of a propane storage sphere and a large vapour cloud formed, ignited and caused a series of BLEVEs.

As described in Chapter 22, the preferred arrangement is the use of a drain line with two valves. The method of operation of these valves is described in *The Storage of LPG at Fixed Installations* (HSE, 1987 HS(G) 34) as follows:

> Particular care should be taken when draining storage vessels in service in order to minimize the escape of LPG. Of the two drain valves, that nearer the vessel, should be fully opened first and draining then controlled by gradually opening the second valve. If, on opening the second valve, no flow occurs, both valves should be closed immediately to allow subsequent investigation. On completion of the draining operation, the valve furthest from the storage vessel should be closed first, then the other valve.

20.15.4 Gas cylinders

There are a number of hazards which can arise from the use of gas cylinders. One of the most frequent types of incident is misidentification of the gas in the cylinder. Thus, for example, oxygen may be used in an application where an inert atmosphere is required. Gas cylinders are marked with an identifying colour code. Common causes of incidents are that the coloured paint has been rubbed off or that people handling the cylinders are not familiar with the code. Cylinders on which the code is not clear should be taken out of service and personnel should be trained to recognize the identification scheme.

Overfilling of cylinders sometimes occurs. This may be due to a defective filling machine or to the use of a machine too small for the cylinder, so that only part of the cylinder rests on the machine.

Cylinders are sometimes heated to give a steady gas supply. There is then the hazard that the isolation valve is turned off and the cylinder explodes. It may be possible, however, to design a cylinder heating system which will not allow the cylinder to overheat sufficiently to cause an explosion, even if the isolation valve is closed accidentally. A suitable system is heating with warm air, the air itself being heated by steam or electricity. Heating of a cylinder by steam or a heat transfer medium is best avoided, because these methods are more liable to cause not only overheating but also corrosion of the cylinder.

The correct method of drawing gas from a cylinder is to set the pressure regulator screw to zero and then to open the isolation valve. Failure to observe this procedure on an oxygen cylinder, for example, can lead to rupture of the regulator diaphragm and an explosion/fire.

With oxygen there is the hazard of igniting materials, such as the plastic caps used to cover the nozzle. Such caps should be entirely removed before the valves are opened.

Another hazard with gas cylinders is that the isolation valve may be damaged in such a way as to allow a rapid flow of gas from the cylinder. In such circumstances the cylinder can become a projectile propelled by the escaping gas.

20.16 Sampling

Sampling is a common cause of accidents to personnel in the chemical industry. It needs to be addressed by the provision of suitable equipment and of formal systems of operation. Accounts of sampling have been given by Ducommon (1964a,b) and Lovelace (1979) and in the ICI *LFG Code*.

Sampling is carried out to monitor product quality, the material balance or equipment operation, or for the purposes of troubleshooting.

A sampling technique should aim to minimize the risk of leakage from the sample point, to safeguard the person taking the sample, to provide a safe means of carriage of the sample to the laboratory and to protect the laboratory personnel handling the sample.

Two principal problems are corrosive liquids and flammable gas and liquids. Before considering these, consideration is given to some general points on liquid sampling.

20.16.1 Liquid sampling

An approach to the safe sampling of liquid streams has been described by Lovelace (1979). He utilizes a proforma for the specification of liquid sampling which covers: the hazards; the sampling conditions, including the frequency of sampling and the size of sample required; any special considerations; the equipment, both installed and portable; and the details of the installed equipment.

The sample point should be treated as a piece of equipment in its own right and designed accordingly. There is no single system which is suitable for all applications.

Sampling systems may be classified as direct or indirect line systems. An ordinary sample valve is a direct line system. Another device is the piston-type sampling valve, in which the sample offtake is set at a 45° angle and is normally kept closed by a piston which moves along the axis of the main sample line. This gives a positive rodding out action and is used in applications where blockage may occur.

In an indirect line system the sample is trapped in a fixed volume and then withdrawn. A simple device which effects this is a sampling plug valve which is installed in line in a pipe. This is a type of ball valve with a sample offtake line and a vent line located in the body of the valve perpendicular to the main pipe, so that when the valve is rotated, the sample trapped in the plug can flow down the sample line. In another type of device the sample is withdrawn using a piston.

A sample chamber is attached directly to the line to be sampled and the liquid is admitted to it by a valve system. One system which minimizes leaks is a double block and bleed valve arrangement.

For syringe sampling use may be made of a septum.

Where sampling can give rise to hazardous fumes, good ventilation is essential. Another method of protection against fumes and leaks is the use of a sampling enclosure, essentially a simple box with the sample pipe entering through the top and the sample bottle

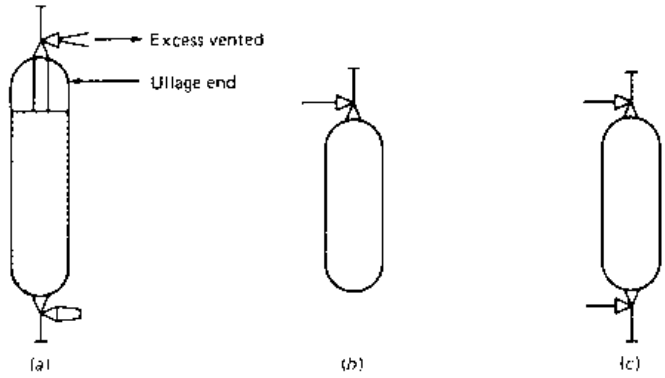


Figure 20.5 *Some sample 'bombs' for liquefied flammable gases (LFGs) (Imperial Chemical Industries Ltd, ICI/RoSPA 1970 IS/74; reproduced by permission): (a) sample bomb for liquids; (b) sample bomb for gases (inlet only); (c) sample bomb for gases (inlet and outlet)*

connection through the bottom. Details of the design of such an enclosure are given by Lovelace.

20.16.2 Corrosive liquids

The following procedure may be used for the sampling of corrosive liquids. The person taking the sample should wear the appropriate protective clothing such as goggles and gloves. The sample bottle should not be held in the hand but on a stand. It is desirable that the sample point be provided with remote operation or with a protective covering around the sample point. The sampler should stand as far as possible from the sample point. If there is no remote operation, he should turn the sample valve using an outstretched arm. The sample bottle should be carried in a bottle carrier.

20.16.3 Flammable fluids

Flammable gases and liquids are usually sampled using a metal bomb. Typical sampling methods are described in the ICI *LFG Code*. For a liquefied flammable gas (LFG) the bomb is a stainless steel cylinder as shown in Figure 20.5(a). A liquid sample is taken as follows. The ullage end of the bomb is connected to the sample point, the bomb is held vertically with the ullage end at the bottom, and both the top and the bottom valves are fully opened. The needle valve is then opened slowly and the bomb is filled. When it is full, liquid emerges from the top valve and all the valves are closed. The bomb is then disconnected from the sample point and inverted so that the ullage end is at the top. The top valve is opened so that liquid issues out until the level in the bomb falls below the bottom of the ullage pipe. When vapour starts to come out instead of liquid, the valve is closed. The ullage for LFG is 20%.

Methods of sampling LFG as gas include (1) evacuation of the bomb before sampling, and (2) purging of the bomb with the gas sampled, the purge being passed to the vent system. Suitable bombs for these two methods are shown in Figures 20.5(b) and 20.5(c), respectively. The ICI *LFG Code* should be consulted for full details of these sampling procedures. Failure to vent a bomb after sampling LFG may result in an explosion if the liquid warms up by heat transfer from the atmosphere. A sample bomb explosion from this cause has been described by Ducommun (1964a).

Ducommun (1964b) also describes a system for avoiding such incidents. The bomb itself is effectively treated as a small pressure vessel, is of special design and is regularly inspected. There is a requirement that the bomb be vented immediately after sampling to give the specified ullage and that this be checked by weighing or other means. The sampling procedure is simple and standardized, personnel are well trained in it and notice of sampling operations is given to the process personnel. The sampling operations are monitored and documented by the laboratory.

20.16.4 Particular chemicals

Certain chemicals require special sampling methods. Techniques for particular chemicals are given, for example, in some of the *Codes of Practice for Chemicals with Major Hazards* by the CIA, such as those for ethylene dichloride and phosgene.

20.17 Trip Systems

Trip systems are provided to protect the plant against certain hazardous situations by shutting it down if particular parameters go outside the specified limits.

There are differences, however, in the extent to which it is essential to provide trip protection with no disarming allowed and in the level to which trip systems can be economically engineered to ensure this. Some trip systems are very sophisticated and provide protection not only during normal operation but also during other conditions such as start-up. In other cases, however, it is necessary to disarm the trip system temporarily to allow the plant to be started up.

Disarming of trips is a permissible practice provided that it is done in accordance with the design intent and with proper procedures. Otherwise, it is an extremely dangerous practice. Probably the most common error is to disarm a trip temporarily, usually during start-up, and to forget to restore it.

The *Flixborough Report* (R.J. Parker, 1975, para. 40) revealed that an automatic system, which initiated safety actions such as shut-off of the air supply and initiation of a nitrogen purge if the level of liquid nitrogen supply fell too low, could be readily overridden by setting to zero the timer for fixing the duration of the purge. Although such action does not appear to have contributed to the explosion, such disarming is a hazardous practice.

If the disarming of trips is to be practised, there should be a procedure which ensures that the trip is correctly restored. Methods used to ensure that disarming is done safely include both key interlocks and permit systems.

If spurious trips occur due to trip initiator unreliability, the operator has an incentive to disarm the trip in order to continue operating, and incidents occur in which operators disarm trips for this reason. Again hardware or software methods may be used to prevent disarming. But it is highly desirable in such cases to improve trip system reliability.

Disarming is not the only way in which a trip can be rendered ineffective. A similar result is often achieved by an alteration of the trip setting. It is equally essential, therefore, to ensure that there is no interference with trip settings.

A trip system should be designed so that it does not reset itself when the trip condition disappears, e.g. valves closed by the trip action should not reopen. It is important, however, that the operations side appreciate the hazards which can arise if the trip system does reset itself. A typical hazard in this case might be the entry of atmospheric air into a vessel filled with hydrocarbon vapours so that an explosive mixture is formed.

20.18 Identification Measures

It is essential, if errors are to be avoided, that plant vessels and equipment be given appropriate marking so that they are readily identified and any hazards associated with them are understood. Equipment identification is of particular importance for maintenance work and is considered in Chapter 21. Here consideration is confined two aspects which particularly concern process operators. These are the identification of hand valves and the labelling of in-plant containers.

20.18.1 Valve identification

One of the principal ways in which the plant is affected by operator actions is through the opening and closing of isolation valves, or hand valves. It is not uncommon for the operator to have difficulty in identifying the right valve, as described in Chapter 14. Yet an error in the identification of a valve can have serious results.

The identification of hand valves is discussed by R. King (1990). A hand valve should be identified on the piping and instrument diagram (P&ID), in the operating manual and on the plant. The P&ID should allow space for the hand valve identification numbers to be inserted; it is often difficult to insert such numbers due to lack of space. The operating instructions should identify hand valves by number.

On the plant a problem arises in maintaining permanent identification of a hand valve. A tag may be put on the valve, but a valve tends to lose its tag or, if it does retain it, it may be removed and put back at some other point. A method which overcomes these difficulties is the marking of the valve number on the pipework, or insulation, with an arrow pointing to the valve in question.

20.18.2 In-plant container labelling

The operation of a process plant can involve the transfer within the plant of a number of chemicals and it is necessary to ensure that these are correctly identified at all times. A programme for the in-plant labelling of containers for such substances has been described by Kmetz (1990).

These containers are those entering the plant, those generated within and retained with the plant, and those leaving the plant. Each container is required to have three pieces of information: the name of the substance, the hazard warning and the party responsible for it.

Employees are responsible for checking that an incoming chemical is labelled. The party initiating shipment is responsible for seeing that an outgoing chemical is labelled and has a material safety data sheet. For in-plant labelling some latitude is allowed. A container used by one person within one shift does not have to be labelled.

20.19 Exposure of Personnel

Of the two main ways of reducing the size of a potential disaster mention has already been made of one, i.e. the limitation of inventory in the process design. The other is the limitation of exposure of personnel in plant operation.

The *First Report* of the Advisory Committee on Major Hazards (ACMH) (Harvey, 1976) suggests that limitation of exposure should be an explicit objective. The *Second Report* (Harvey, 1979b) gives guidelines for the limitation of exposure.

The hazard to which personnel are exposed may be a large fire, an explosion or a toxic release. Various scenarios for such hazards should be reviewed so that zones in which exposure is controlled can be delimited on a rational basis.

Exposure is most simply limited by not having people there in the first place. For those whose presence is essential much may be done to provide protection, particularly through the siting and design of buildings. This latter aspect is discussed in Chapters 10 and 24. Only the reduction in the numbers present by management control is considered here.

Typically, a large process plant has a number of shift process operators who man the control room and work about the plant opening and closing valves, changing pumps, replacing filters, taking samples and performing various other tasks. Some operators spend most of their time in the control room, others are mainly out on the plant. There are also several shift mechanical and instrument maintenance fitters. All these personnel patrol the plant and observe any abnormalities such as leaks or spillages and they are available to deal with plant upsets. Laboratory personnel also go out on to the plant to take samples for analysis.

In general, the numbers of shift operating and maintenance personnel on modern process plants are already at the minimum level consistent with safe and

efficient operation. In most cases further reduction would make it difficult to deal with emergency situations.

During the day there is a rather larger number of maintenance personnel on the plant. The plant manager and the plant engineer are also on the plant during the day time. In addition, there are often other technologists concerned with carrying out investigations of all kinds.

If a plant extension is being carried out, there will also be a fairly large number of construction personnel on the plant or very near it.

The numbers of men on a large process plant might be expected to be approximately as follows:

Shift operating personnel	5–25
Shift maintenance personnel	0–5
Day maintenance personnel	10–100
Managers, technologists	2–10
Construction workers	10–50

In the event of an emergency, the shift personnel have specific instructions on the action which they should take and on the alarm or other instruction at which they should evacuate. The order to leave the plant is given to the day maintenance personnel and to construction workers on the appropriate alarm signal or on instruction from their respective supervisors.

For the purposes of limitation of exposure, personnel may be divided into the following categories of exposure in the hazard area:

Category 1 Continuous exposure (e.g. process operator).
Category 2 Intermittent exposure:
(a) short periods (e.g. technologist);
(b) infrequent long periods (e.g. fitter).
Category 3 Infrequent exposure (e.g. accounts clerk).

The works site may be divided up into areas of (1) major hazard, (2) intermediate hazard, and (3) low hazard.

The limitation of exposure of personnel is effected by controlling (1) permanent location and (2) movement.

The number of people permanently located in a major hazard area should be kept to a minimum consistent with safe and efficient operation. In particular, personnel in Category 2 should be there only if their presence is essential, as opposed to merely convenient. Examples of such personnel include technologists, training officers, maintenance planners, laboratory analysts and clerical assistants.

Personnel usually located in the intermediate hazard area include maintenance and other services. Again the number should be kept as low as is reasonably practicable.

Personnel should be given protection by suitably designed buildings, as described in Chapter 10. In the major hazard area the main protective building is the control room. The type of protection afforded by this will depend on the nature of the hazard (fire, explosion or toxic release). Buildings in the intermediate hazard area should also offer some protection. The ACMH suggests that personnel exposed to this intermediate level of hazard should have a work base such that they would not expect to be seriously hurt. Buildings such as the site office should be in the low hazard area, but should still be designed to minimize injury.

The other main control is on movement. There should be formal procedures, including a permit system for entry into the major hazard area. This permit system should be enforced and audited. The procedure should ensure that the number of people in the major hazard area is considered and that their identity is known at any given time.

It is particularly important for the system to afford good control of situations such as major plant construction and modification, in which there may be quite large numbers of people in the major hazard area. It should be borne in mind that the presence of a large construction team, who are relatively unfamiliar with the plant, is in itself a further cause of hazard.

20.20 Security

Another important aspect of plant operation is security. This is treated in *Vandalism* (C. Ward, 1973), *Introduction to Security* (G. Green and Farber, 1974) and *Industrial Security* (D.L. Berger, 1979). The *Compendium of Fire Safety Data* (FPA, 1992) contains a section on security precautions (the SEC series). Accounts are also given by Hamilton (1967), Oliver and Wilson (1972), K.G. Wright (1972), Spranza (1981, 1982, 1991, 1992) and Pitt (1987).

Security systems management is described by Spranza as being essentially a blend of traditional security concepts and modern management methods.

The management system should include an explicit requirement for a review of the security system. This review should cover both hardware and software aspects and should involve a critical examination in which problems are identified, alternative solutions are generated, and a suitable approach is selected and implemented.

In assessing the security problem the categories of person who need to be considered include employees, visitors and intruders; the types of behaviour to be considered include innocent actions, theft and malicious acts.

Central to security is control of access. The security system should ensure that unauthorized persons do not have access to the site, whether or not they have hostile intent. The minimum requirement is a formal pass system which covers employees and visitors. There then needs to be physical arrangements to ensure that access to the site is controlled at all points. This aspect of security is clearly related to plant layout and is considered in Chapter 10. The *Flixborough Report* found that, although in general proper attention was paid to security, there were two unguarded gates through which it was possible for anyone at any time to gain access to the site.

In addition, it may be necessary to exercise control of access to particular areas within the site.

It is also desirable for the operational system to be capable of detecting the presence of any unauthorized persons who do get onto the plant. The patrolling of the plant by the process operators is relevant here. So also are formal arrangements for the limitation of exposure of personnel by the control of access to major hazard plant.

With regard to intruders, there are available various devices which may be used to give warning. Good lighting is one obvious feature. Other measures include

detectors buried in the earth between two fences, heat sensitive detectors and closed circuit TV cameras. The use of some devices may, however, encounter difficulties on process plant, such as those due to heat radiation from the plant itself.

Another basic principle of security is to create conditions which assist in the rapid detection of any unauthorized deviation. A simple illustration is the maintenance of tidy storage of laboratory chemicals, so that a missing item is readily detected. But the principle is of much wider application.

Some facilities have their own characteristic problems with regard to security. Those of storage are described by Pitt (1987). One common defect is access by unauthorized vehicles. Other defects occur in drum and cylinder storage, where drums are often placed too close to the boundary fence and cylinders are left all over the place. The particular problems of security in laboratories, also discussed by Pitt, are considered in Appendix 9.

The most difficult security problem is a deliberate attack by well trained and organized saboteurs. Defence against such an attack is a matter for the military which is outside the scope of this book. There are several things, however, which can be done to make such an operation more difficult. The potentially more vulnerable units can be sited away from the periphery and can, to some extent, be designed to limit the damage caused by explosives, and an effective security system can reduce the amount of material which a saboteur can bring in and the time which he can spend on his task.

The security problem is not confined to outsiders, however; the threat not infrequently comes from the company's own employees. Theft by employees can in some cases pose a threat to the plant, particularly where there are high priced materials which it may be attractive to steal. The sort of incident which occurs and which may have safety implications is the theft of sections of copper cabling carrying the power supply to electric motors while the plant is shut down.

More serious interference by employees may involve sabotage or arson. Arson is one of the causes of fire on process plants considered in Chapter 2. The *Compendium of Fire Safety Data* (FPA, 1992) contains an 'arson dossier' (the AR series). Arson is one of the topics dealt with in the *NFPA Handbook* (Cote and Linville, 1986).

The effective operation of a security system requires that all involved are fully trained so that they understand what the functions of the system are, how it works, what their own role is and how they should discharge it.

20.21 Notation

Section 20.3

C	interface concentration (ppm)
H_s	heat of solution (cal/gmol)
k	constant
ϕ	fractional humidity (% relative humidity/100)

Section 20.14

d	diameter of tank
F_1, F_2	forces defined in Figure 20.2(a)
ΣF	vector of forces defined in Figures 20.2(b) and 20.2(c) for positive and negative internal pressures, respectively
p	pressure
r	radius of tank
t	thickness of tank wall
α	angle defined in Figure 20.2(a)
δ	width of element in Figure 20.2(a)
σ_b	bending stress in tank roof
σ_h	hoop stress in tank wall
σ_s	shear stress between tank roof and wall
ϕ	angle defined in Figure 20.2(a)

21 Plant Maintenance and Modification

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21.1 Management of Maintenance

The need for maintenance on a plant implies some abnormality and often some increase in hazard. The conduct of the maintenance work may also introduce its own hazards to the plant. In addition, the maintenance activities may be a hazard for the personnel involved in them. It is necessary, therefore, to exercise careful control of maintenance work in order to eliminate hazards to the plant and to the personnel.

The consequences of failure to exercise this control can be serious. The Piper Alpha disaster was caused by failures in isolation procedures, the permit-to-work system and the handover system associated with maintenance work.

Some work constitutes modification rather than maintenance. In previous chapters emphasis has been placed on the need to maintain the integrity of the plant. This integrity may be degraded by plant modifications unless they are closely controlled. The Flixborough disaster was judged to have been caused by a modification which reduced plant integrity.

Thus both plant maintenance and plant modification require systems of control with a fairly high degree of formality. Plant maintenance needs to be administered through some kind of permit system, while plant modification requires a system which identifies, checks and records modifications.

The safe maintenance of process plant is dealt with in *Safety in Inspection and Maintenance of Chemical Plant* (BCISC, 1959/3), *Safety and Management* (ABCM, 1964/3), *Permit-to-Work Systems* (CAPITB, 1977 Inf. Pap. 16A), *Refining Safety Code* (IP, 1981 MCSP Pt 3), *Deadly Maintenance* (HSE, 1985b), *Liquefied Petroleum Gas*: vol. 1, *Large Bulk Pressure Storage and Refrigerated LPG* (IP, 1987 MCSP Pt 9) (the IP *LPG Code), Guidance on Permit-to-Work Systems in the Petroleum Industry* (OIAC, 1991) (the OIAC *Permit Systems Guide*) and *Maintenance of Process Plant* (the IChemE *Maintenance Guide*) (Townsend, 1992). Selected references on plant maintenance are given in Table 21.1.

21.1.1 Safe systems of work

The requirement of the Health and Safety at Work etc. Act (HSWA) 1974 for safe systems of work is particularly relevant to the maintenance of process plant, where there are many jobs which involve degree of potential hazard, but which can be done safely provided proper control is exercised. It is also characteristic of maintenance that it often involves quite a large number of people and that systems to ensure good communications are important.

Basic elements of the overall safe system of work are: written procedures for non-trivial tasks; documentation of these procedures and of the equipment; the permit-to-work and handover systems; systems for control of a large workforce and for dealing with contractors; and supervision and training.

21.1.2 Maintenance procedures

Any regular maintenance task which is non-trivial should be governed by a formal written procedure. This procedure should address the specific task and should complement the general permit and handover systems described below. In particular, there should be formal

Table 21.1 *Selected references on plant maintenance*

Plant maintenance, general (see also Table 7.1)
NRC (Appendix 28 *Maintenance*); NSC (Safe Practice Pmphlt 70); L.C. Morrow (1957); F.L. Evans (1962); MCA (1962–/1–4); J.E. Miller and Blood (1963); H.V. Stewart (1963); Goldman and Slattery (1964); Newborough (1967); Blanchard and Lowery (1969); IMechE (1969/2, 1975/19); Iron and Steel Institute (1969); J.R. Hughes (1970); HSE (HSW Bklt 28); Jardine (1970a,b, 1973); Cunningham and Cox (1972); G.H. Mitchell (1972); Gradon (1973); B.J. Lewis and Low (1973); D.J. Smith and Babb (1973); E.N. White (1973); Clifton (1974); Elonka (1975); Lees (1975); Husband (1976); Priel (1974); Corder (1976); Higgins and Morrow (1977); A. Kelly and Harris (1978, 1983); Nertney (1978); Buffa (1980); Worrall and Mert (1980); API (1982/3); D.J. Smith (1981, 1991); Blackney (1982); Rosaler and Rice (1983); Hickman and Moore (1986); A. Kelly (1986); Langley (1986); McAlister (1986); G.T. Edwards (1987c); A. Hunt (1989); Dunlop (1990); T.A. Henry (1990); Hirata (1990 LPB 96); File (1991); Parkinson (1991)

Human factors in, and training for, maintenance
NRC (Appendix 28 *Maintenance Personnel Reliability Model*); Landeweerd and Rookmaaker (1980); Nawrocki (1981); Spiker, Harper and Hayes (1985)

Terotechnology
DoI (n.d./1, 1975/2–6, 1976/7, 1977/8, 9); IMechE (1973/6, 1975/21); Tracht (1964); R.P. Reynolds (1974, 1976); J.A. Richardson (1976); Berg (1977); Rappini *et al.* (1977); Parkes (1978); K. Lewis (1979); Partington (1980)

Design-out of maintenance, design for maintenance
Alford (1965); Constable and Parkes (1979); Lieberman (1979)

Plant maintenance, process industries
BCISC (1959/3); Staniar (1959); Signorini (1961); F.L. Evans (1962, 1967, 1969); Dodds (1963); Roughley (1963); ABCM (1964/3); Stratmeyer (1964); Alford (1965); Elgee (1965); D.T. Smith (1965b); Verseput (1965); H.R. Carter (1966); E. Johnson (1966); Matley (1970); Trotter (1970, 1973); Cason (1971); Hodnick (1971); Jumper (1971); Virgils (1971); Anon. (1972d); Finley (1972, 1973, 1978, 1987); C.F. King and Rudd (1972); Nowlan (1972); *Chemical Engineering* (1973b); McCullough (1973); Husband (1974, 1976); A. Kelly (1974, 1980, 1981, 1986); H.S. Moody (1974); Snyder (1974); Warburton (1974); Anon. (1975 LPB 39, p. 8); Anon. (1975 LPB 4, p. 9); Goyal (1975); Harris and Kelly (1975); Roseman (1975); Bosselaar (1976); Husband and Basker (1976); Piper (1976); Anon. (1977 LPB 14, p. 2); Balaam (1977); Bollinger and Wright (1977); Innes (1977); Mann (1977); Wanner (1977); Buttery (1978); A. Davies (1978); R. King and Magid (1979); Marre and Reichert (1979); Vargas (1979, 1980a,b); Chamberlain (1980); *Chemical Engineering* Staff (1980); J.D. Edwards (1980); Iverstine and Sturrock (1980); Schmid (1980); Chandler and Brooks (1981); Creaney (1981); Hellhake (1981); Seddon and Kelly (1981); Hay (1982); Kirby (1982); de Matteis (1982); D.T. Smith (1982); API (1983 Publ. 2007); Charlton and Huitson (1983); A. Kelly and Harris (1983); Wilkie (1985b); Baguley (1986); Langley

(1986); Tropp (1986); Deacon (1988); Riance (1988); T.A. Henry (1990, 1993a,b); Hirata (1990); Ng Tong Leng (1990); FM Int. (1991a); Gans, Kohan and Palmer (1991); Godse (1991); Moubray (1991); Snow (1991); M. Taylor (1991); Anon. (1992 LPB 104, p. 12); Crawley (1992 LPB 102); Mundy (1992); Townsend (1992); Vouets (1992); S.C. Leonard (1993); Worledge (1993); Hulme (1994)

Contract maintenance
J.H. Jordan (1968); Sarappo (1969); C.J. Carter (1980); Whitaker (1993)

Life cycle costing, replacement decisions
Anon. (1961c); Munro (1963); Fisher (1963); J.P. Epstein (1967); J.R. Hughes (1970); Maristany (1968); Jelen and Cole (1971); Fair (1973, 1974); Finley (1973); Anon. (1974f); Perkins (1975); Jelen and Yaws (1977); Parkes (1978); J.L. James (1979); Lees (1983b); Grundfos Pumps (1984)

Revalidation, remanent life assessment
ASME (1980/81, 1983/89, 1986 PVP 112, 1987 PVP 129, 1988 PVP 138, 1989 PVP 171, 1991 B31G); Zeis and Eschenbrenner (1980); Baker-Counsell (1987b); Grosshandler (1987a); British Gas (1990 Comm. 1438, 1439); Baas and Warner (1992)

Computer-based systems
Eason and White (1977); Beatson (1978); Trotter (1979); Redding (1980); McChrystal (1982); Anon. (1987c); Grosshandler (1987a); Collington (1989); Anon. (1990b); Project Software and Development Inc. (1991)

Particular equipment
Foundations: Renfro (1975, 1978, 1979); Vick, Witthaus and Mayo (1980)
Gas plant: IGasE (1987 IGE/TD/11)
High pressure plant: McClelland (1968); Andrews and Weber (1993)
Electrical equipment: Autenriet (1962); Erb (1975); HSE (1980 HS(G) 13); NEPA (1990 NFPA 70B)
Pipework: McNaughton (1979)
Heat exchangers: Yokell (1983); Stegelman and Renfftlen (1983); Fijas (1989); Pugh *et al.* (1993)
Steam traps: Isles (1977)
Valves: Kletz (1984l); Charbonneau (1985); Irhayem (1985); Anon. (1989 LPB 85, p. 1 and 3); Anon. (1989 LPB 87, p.9) in Anon. (1992 LPB 103, p. 25 and 29); Anon. (1992 LPB 107, p. 27)
Heaters: Goyal (1967); Sharp (1977)
Combustion systems: R. Fletcher (1979)
Flare stacks: Anon. (1992 LPB 107, p. 23)
Machinery: W.E. Nelson (1974, 1980); L.D. Martin, Young and Banks (1977); Houghton (1979); Vargas (1982); Murray (1983); Parry (1990); Gresh (1992); Rutan (1993)
Pumps: Love (1972); R. James (1976); Yedidiah (1974, 1977); Grundfos Pumps (1984); French (1992); Bitterman (1993); Pradhan (1993)
Power transmission: G.W. Howard (1971, 1977)
Pressure relief valves and systems: Lortz (1966); Woolfolk and Sanders (1984, 1987); J.K. Rogers (1988); Duckworth and McGregor (1989); Coulston (1993)
Instrumentation: Sherman (1960); Upfold (1971); Barbin (1973); IP (1980 MCSP Pt 14); Hasselbaum (1992)
Vessels: Megow and Dawson (1977); Snow (1979); R.S. Brown (1982); Quraidis (1982); Pritchard (1983); Guth and Clark (1985)
Tanks: H.V. Bell (1982); Shtayieh (1983a,b): Huston (1983)
Bunds: Hazen (1991)
Chlorine systems: BCISC (1975/1); Chlorine Institute (1975 Publ. 41, 1981 Publ. 42, 1982 Publ. 39)
LPG systems: LPGITA (1984 LPG Code 14,1986 LPG Code 1, Pt 3)
Fire protection equipment: MCA (SG-13); FMEC (1986 LPB 71); NFPA (1987 NFPA 13A, 1993/33)
Pipelines: McNaughton (1979); P.M. Scott and Kiefner (1984); AGA (1990/69); IGasE (1990 IGE/SR/18, IGE/ER/1); API (1993 RP 2200)

Used equipment
J.P. Epstein (1967, 1978); C. Butcher (1992d, 1993a)

Unused equipment, dead ends
Anon. (1983 LPB 49, p. 28); Kletz (1989 LPB 87)

Mothballing
Twigg (1985); R.G. Miller and King (1987); Savage, Portnoy and Parkinson (1988)

Permit systems
ROSPA (n.d./1); BCISC (1959/3); ABCM (1964/3); O'Driscoll (1965); J.R. Hughes (1970); CAPITB (1977 Inf. Pap. Suppl. 16A); IP (1981 MCSP Pt 3, 1987 MCSP Pt 9, 1993 TP 11); Kletz (1982f); Anon. (1984 LPB 55, p. 11); HSE (1986 IND(G) 39(L), 1992 IND(G) 98(L)); V.C. Marshall (1986b); Trowbridge (1987); OIAC (1986, 1991); Anon. (1989 LPB 85, p. 3); FPA (1989 CFSD GP 3); Anon. (1990 LPB 92, p. 7, 10, 18 and 21); Anon. (1990 LPB 93, p. 32 and 35); British Gas (1990 BG/PS/G11); Cullen (1990); Anon. (1992 LPB 104, p. 5); Anon. (1992 LPB 107, p. 27); S. Scott (1992); Townsend (1992); Anon. (1993 LPB 112, p. 20); Butler and Bonsal (1993)

Interlocks
Anon. (1983 LPB 49, p. 7)

Maintenance activities
Bolting: NRC (Appendix 28 *Bolts*); British Gas (1979 TIN10); K. Gibson (1986); Bett (1989); Davie (1989); Ritchie (1989); Standen (1989); Whalley (1989); Garner (1993)
Equipment isolation: Anon. (1990 LPB 91, p. 17); Anon. (1990 LPB 92, p. 19)
Line breaking: BCISC (1959/3)
Blockage clearing: Anon. (1990 LPB 92, p. 9); Anon. (1991k)
Lifting, rigging: N.L. Owen (1965); van Amerongen (1968, 1970); Mallinson (1968); EEMUA (1984 Publ. 101)
Manholes: Bond (1987 LPB 78)
Vessel entry, entry into confined spaces: MCA (SG-10, 1962–/1–4); SMRE (*Gas detection* 1, 2, 4, 10); BCISC (1959/3); ABCM (1964/3); Wareing (1969); DoEm (1971/1); Huggett (1973); HSE (1974 TDN 46, 1975 TDN 47, 1977 GS 5, 1991 Construction Sheet 15); Anon. (1975 LPB 3, p. 8); FRS (1975 Fire Res. Note 1044); NIOSH (1979 Crit. Doc. 80-106, 1987 Publ.

87–113); Anon. (1980 LPB 31, p. 11); Burnett (1980); Anon. (1983 LPB 53, p. 15); Anon. (1984 LPB 56, p. 26); API (1984 Publ. 2217, 1987 Publ. 2217A); Bond (1984 LPB 59); Anon. (1985 LPB 63, p. 31); Kletz (1985b); Keller (1987); IGasE (1987 IGE/SR/5); Anon. (1988 LPB 81, p. 29); Anon. (1991 LPB 98, p. 19); Anon. (1992 LPB 102, p. 27); Crawley (1992 LPB 104); NFPA (1993 NFPA 326); Suruda *et al.* (1994)

Tank cleaning, repair and demolition: Anon. (n.d.a); API (1981 *Guide for Inspection of Refinery Equipment* Pt 13, 1981 Publ. 2015B, 1982 Publ. 2015, 1983 Publ. 2200, 2202, 1985 Publ. 2015, 1988 Publ. 2027, 1991 Std 653, Publ. 2013, 1993 Std 2015); HSE (1970 HSW Bklt 32, 1975 TDN 18, 1985 CS 15); Barrell (1971); Associated Octel Co. (1972 Bull. 20, 1975 Luckritz and Schwing (1973); (1075 Bull. 28), FRS (1975 Fire Res. Note 1044, 1977 Fire Res. Note 1074); Savage (1975); Fardell and Houghton (1976); Amey (1977a,b); A.A. Briggs (1979); Vick, Witthaus and Mayo (1980); IP (1989 MCSP Pt 16); Jacob (1990); Moros, Howells and Ryall (1993); NFPA (1993 NFPA 327)

Welding, hot work: AWS (Appendix 28, 1976/1, 1978/2, 1992/13); ASTM (STP 11, 494); IRI (n.d./2); NSC (Safe Practice Pmphlt 105); Welding Institute (Appendix 28, 1981/35, 36, 1986/38, 1991/43); API (1988 Publ. 2009, 1991 RP 1107); BCISC (1959/3); Voelker (1965, 1973); Sanderson (1969); HSE (1970 HSW Bklt 38, 1978 M 15, 1979c, 1979 HS(G) 5, IND(G) 35(L), 1986 PM 64, 1989f); Voelker and Zeis (1972); Eales (1977a); A.J. Williams and Mallone (1977); Eutectic and Castolin (1979); R. King and Magid (1979); Schell and Matlock (1979); Anon. (1980 LPB 32, p. 15); CGA (1981 SB-8); AIHA (1984/6, 8); Nock (1985); NIOSH (1988 Crit. Doc. 88-110); FPA (1990 CFSD GP 2); Gregory (1990); Balchin (1991 Welding Institute/12); Stippick (1992); ANSI Z49.1-1988; BS (Appendix 27 *Welding*)

Onstream repairs: API (1978 Publ. 2209); Bloom and Pebworth (1979); G.W. Harrison (1980); Anon. (1988l); Pennington (1992)

Leak repair: Hutton (1973); Stroud (1981); Barsness (1982); Maushagen (1984 LPB 55); Anon. (1986n); Bond (1986 LPB 69); J.K. Rogers (1988)

Hot tapping: Hahn, Brownlee and Thompson (1969); de Hertogh and Illeghems (1974); Britt (1975); Elder and Batten (1975); Hahn (1975); W.B. Howard (1975a); Howden (1975); Letchford (1975); Warren (1975a); API (1985 Publ. 2201, 1991/19); AGA (1988/57, 1989/61)

Cleaning with water, chemicals: C.T. Fox (1967); Engle (1971); Loucks (1973); Vanmatre (1977); Roebuck (1978); Anon. (1980 LPB 35, p. 7); Anon. (1981 LPB 38, p. 23); Shorthouse (1983); Hyde (1985); Donaldson (1986); HSE (1988 PM 29); Junique (1988); J.O. Robinson (1993)

Cleaning in place: Kirkland (1986); Someah (1992)

Water jetting: High Pressure Water Jetting Contractors (1982)

Decontamination: Dransfield and Greig (1982); EEMUA (1989 Publ. 154)

Maintenance equipment

HSE (Appendix 28 GS, PM series)

Tools: EEUA (1958 Doc. 4); Anon. (1962e); IGasE (1970/9); FPA (1975 S11); Kletz (1977i); HSE (1978 PM 14, 1990 PM 32); R. King and Magid (1979); Anon. (1984j); API (1989 Publ. 2214)

Lifting equipment: ICI/RoSPA (IS/102); SMRE *(Engineering Metallurgy* 2, 3, 5); Bates (1992); BS (Appendix 27 *Lifting Equipment*)

Scaffolding: DoEm (1974/5); Anon. (1989 LPB 89, p. 9 and 18); BS 5973: 1990

Cranes: RoSPA (IS/29); HSE (1973 TDN 26, 1974 TDN 27,1976 PM 3, 1979 PM 9, 1980/11, 1985/17); Aitken (1987); BS (Appendix 27 *Cranes*), BS COP 3010: 1972

Forklift trucks, power trucks: MCA (SG-6); RoSPA (IS/38; Rochester (1969); Partridge (1977); HSE (1979 HS(G) 6); NFPA (1992 NFPA 505)

Engine-driven equipment: API (1987 Publ. 2203)

Robots: Collins (1982); IMechE (1982/62); T.J. Williams (1983); Siddle (1986b); Mitler (1989); R.M. Taylor and Lewis (1987); HSE (1988 HS(G) 43); NIOSH (1988 Publ. 88–108)

Maintenance hazards

HSE (1985 PML 7, 1985/16, 1987/20, 1992 HA 1, 1992/30)

Construction, demolition

Construction: HSE (HSW Bklts 6A–6F, 1983 GS 24, 1984 GS 28, 1985 GS 33, IND(G) 30(L), 1991 Construction Sheet 15, GS 6); Hayward (1969); Oil and Chemical Plant Constructors Association (1974); National Federation of Building Trades Employers (1975); RoSPA (1975 IS/13); ES 6187: 1982

Construction equipment: HSE (1981 PM 27, 28, 1982 GS 15, 1983 PM 30, 1984 GS 31, 1987 G5 42)

Demolition: Stuart (1974); Oberhansberg (1977); HSE (1989 GS 29); Anon. (1992 LPB 104, p. 10); BS 6187: 1982

Construction, demolition hazards

HSE (1981/2)

procedures for the installation and removal of slip plates and blind flanges. The principles underlying the writing of operating procedures are applicable in large part to maintenance procedures also.

21.1.3 Maintenance documentation

These maintenance procedures should be supported by the necessary documentation. This should include documentation on the procedures themselves, the piping and instrument diagrams, the instrumentation and electrical system diagrams, and specialist documentation. This should include diagrams of the plant showing points at which slip plates, etc., can be inserted, and lists of the slip plating required for isolation for particular purposes. The documentation, whether procedures, diagrams or records, should be kept up to date.

21.1.4 Permit system

Maintenance work should be governed by a formal permit-to-work system. The purposes of such a system are: to see that proper consideration is given to the job, its hazards and the precautions required; to ensure that these are understood by all persons involved; and to

facilitate effective communication between the parties concerned.

The permit system is intimately bound up with the hazards of maintenance and with the various preparations and precautions required to make a plant safe for maintenance work. These are therefore described first and the permit thereafter in Section 21.8.

21.1.5 Handover system

The permit-to-work system should be complemented by formal shift handover procedures. These procedures are described in Chapter 20 with particular reference to handover between operators, but essentially similar considerations apply to the maintenance function.

21.1.6 Control of workforce

The workforce involved in maintenance and related work may be quite large and varied. The core maintenance workforce of company employees may be supplemented by contractors working on routine maintenance and on equipment testing and recertification. In addition to the workforce thus engaged there may well be extended periods when other plant modification or extension work is going on involving in total a considerable number of people. All this work needs to be controlled through the permit system. The need to exercise control may in some cases set a limit on the volume of work which can be undertaken.

21.1.7 Contractors

As just indicated, a portion of the workforce engaged in maintenance work may be contractors. The trend in recent years has been towards increasing use of contractors, not only on construction work but also on more routine jobs such as equipment testing and recertification. The reasons for the use of contract maintenance are discussed by C.J. Carter (1980) and the identification and control of contractor hazards are described by Whitaker (1993).

There should be a system of quality assurance for work to be put out to contract. It is normal to require the contractor to provide evidence of the quality of his work, supervision and training, and of his own quality assurance procedures. Visits are paid to the contractor to check on these matters.

In some cases a contractor's personnel may work on a site for years on end and become as familiar with the systems as company personnel, but in others they may be there for quite a short time. In any event, it is necessary that before new personnel from a contractor start work they are properly trained in these systems.

The need for this was highlighted by the Piper Alpha disaster, where a two-man team of contractors was carrying out testing and recertification work on pressure relief valves on the platform, but the senior of the two was on his first tour as supervisor and had not received adequate instruction in the permit system.

21.1.8 Supervision and training

It will be evident that supervision and training are essential in ensuring that maintenance work is done safely. The permit and handover systems provide a structure for the supervision of maintenance work, but by no means exhaust the contribution of supervision.

With regard to training, maintenance personnel should be trained not only in their own craft, but also in the hazards of the chemicals and the plant, the jobs which they do such as isolation and vessel entry, in the permit and handover systems, and in making the distinction between a routine maintenance task and a modification. The training of maintenance personnel is considered further in Chapter 27.

21.2 Hazards of Maintenance

As already stated, maintenance work on process plant involves a number of hazards. An account of maintenance hazards and accidents is given in *Deadly Maintenance* the (HSE, 1985b), *Dangerous Maintenance* (HSE, 1987a) and HS(G) 49 *Human Factors in Industrial Safety* (HSE, 1989), and by Deacon (1988).

The first of these is a study by the Accident Prevention Advisory Unit (APAU) of the Health and Safety Executive (HSE) of maintenance accidents in British industry during the period 1980–82. In this period there were over 100 deaths per year caused by maintenance work, and over the 3-year period there was a total of 106 deaths (33%) associated with the maintenance of plant and machinery. The fatalities were assigned to the following categories: breakdown and scheduled maintenance work 66%; cleaning 25%; and examination, lubrication, painting 9%. A feature of these statistics is the prominence of accidents in cleaning.

Although maintenance craftsmen comprised the largest single category of deaths (37%), fatalities to operators were almost as numerous (33%). Other groups included labourers (7%), service engineers (6%), and managers, supervisors and proprietors (13%). The relatively large number of deaths among operators is accounted for only in part by cleaning operations.

The accidents were classified by equipment type, accident type and major cause. There were 66 accidents assigned to identified categories of machinery and 32 to identified categories of plant, the balance of 8 being assigned to machinery and plant in general. Of the machinery accidents, 23 were caused by conveyors and elevators, but few of the others identify process machinery. The breakdown of plant accidents is: storage tanks, 7; furnaces and associated plant, 6; boilers, heating and ventilation plant, 5; chemical, gas, oil, process plant, 5; dust or fume extraction plant, 5; and degreasing tanks 4.

The classification by accident type is: machinery, 50, of which 17 involved entanglement and the rest some form of crushing; falls, 21; burns, 10; gassing, 9; electrocution, 6; asphyxiation, 5; and struck by falling materials or plant, 5.

By major cause the classification is: absence or failure of system of work, 35; absent or defective equipment, guards or working platforms, 23; failure of management organization or supervision, 11; inadequate or lack of training, instruction or information, 8; human error, 10; unauthorized activity, 5; defective design of plant or machinery, 5; and unknown or unforeseeable incident, 9.

The authors present three case studies of generic types of accident, associated with (1) conveyors and elevators, (2) overhead travelling cranes and (3) confined spaces.

The APAU publication also contains some 99 case histories of accidents in maintenance work. Other specialized collections include *Safety in Maintenance* (API, 1981 Safety Digest 4) and that given by Kletz (1982f), whose other work is also replete with maintenance case histories. Maintenance work also features strongly in many general collections of case histories.

Confined spaces present a number of hazards, and these are described in Section 21.7. Other hazards are mentioned throughout this chapter.

21.3 Preparation for Maintenance

There are a number of preparatory measures which may need to be taken before maintenance work is started. The principal means of control of such work is the permit-to-work system. The preparatory measures to be taken should be specified on the permit.

Many of these measures are aimed at allowing work inside plant to be done safely. If work is to be done internally on an item of plant, it should be prepared by the following operations: (1) depressurization, (2) cooling down, (3) isolation, (4) removal of contents (gas, liquid, solids) and (5) cleaning.

21.3.1 Identification of plant

Many incidents occur on process plant due to errors in the identification of the equipment on which work is required. Plants can often seem a confusing maze of vessels and pipework, much of it lagged, and it is often difficult to identify equipment unaided simply by tracing the course of pipework or by the use of other clues. This point has already been made in Chapter 14 in relation to the work of the process operator. It is necessary, therefore, to adopt a more positive policy for the identification of equipment.

One method which may be used is to attach a permanent identification to a particular equipment. This is an effective system provided precautions are taken against certain types of error which can occur.

There are certain standards and codes of practice for the identification of equipment. In particular, mention may be made of BS 1710: 1984 *Specification for Identification of Pipelines and Services*.

Identification should be consistent and should accord with reasonable expectations. It is asking for trouble, for example, to number unsequentially equipments which form a natural sequence, such as pumps in parallel or reactors in series. Another situation to be avoided is ambiguity as to which of two adjacent equipments an identifier refers to.

Much maintenance work involves breaking into pipe joints. Permanent identifiers are not as suitable in this case. Another method of identification, therefore, is the identification tag. This is particularly useful for joints, but is applicable to other equipments also instead of permanent identification.

The identification of pipe joints is particularly important, because incidents are frequent in which the wrong joint is broken. Many such occurrences could be avoided by a positive system in which the identification tag is put on the joint to be broken.

For the type of work described a permit-to-work is required. The identification of the equipment, whether permanent or temporary, should be given on the permit form.

The system described is not foolproof, of course. The person putting the identification tag on the equipment can make a mistake. But in general it does appear to be an effective system in practice.

The use of the identification tag system is preferable to merely pointing out to the maintenance fitter the equipment to be repaired. Incidents have occurred which suggest that this is not always adequate.

21.3.2 Depressurization

If the plant contains liquid heated above its boiling point under pressure, it may be necessary to let it cool down prior to depressurization in order to avoid excessive flash-off. Depressurization should be performed in accordance with the design intent. For flammable or toxic gases this should preferably be to another part of the process. Alternatively, it may be to flare, to a scrubber system, or in some cases to the atmosphere. For inert gases venting is often to a vent stack or vent pipe.

21.3.3 Cooling

If the plant has not already been cooled down sufficiently prior to depressurization, it should now be cooled down. Cooling involves the hazard of vacuum collapse. This may be guarded against by inert gas injection to maintain the internal pressure at atmospheric pressure.

21.3.4 Isolation

When the plant has cooled down, the equipment to be worked on should be isolated. This includes isolation of vessels and pipework from process and utility fluids, isolation of machinery from its power sources, and isolation of electrical equipment. Isolation is crucial both to the safety of the plant and to that of the personnel. It is considered in detail in Section 21.4.

21.3.5 Emptying of liquids

Once the plant has been isolated, the next step is to remove its contents. If it contains liquid, this is usually pumped away to another part of the plant or to storage, or, if non-hazardous, to drain. The liquid may leave behind hazardous residues, which are considered in Section 21.3.7.

21.3.6 Gas freeing

If the contents of the plant are gas or vapour, there are a number of methods of gas freeing which may be used to replace them with air. These methods include (1) forced ventilation, (2) flushing with water and forced ventilation, (3) purging and (4) steaming.

As already described, a plant often contains flammable or toxic residues. If these are sufficiently volatile, they may constitute a continuous source of contamination.

The choice of method of gas freeing depends on the type of plant, on its initial contents, including residues, and on the work to be done. Where steaming is used for cleaning, gas freeing occurs at the same time.

Purging is discussed in Section 21.5 and other methods of gas freeing are described in relation to tank cleaning in Section 21.12. An account of the gas freeing of crude oil storage tanks is given by Moros, Howells and Ryall (1993).

21.3.7 Removal of solids

Solid process materials include raw materials and final products, and catalysts and adsorbents. Raw materials are often removed by continuing to run the process until they are exhausted. Products, catalysts and adsorbents are generally transferred to suitable containers.

There are a number of hazards associated with solid process materials which need to be guarded against. Solid materials may be flammable, toxic or pyrophoric. Flammable dusts may give rise to a dust explosion. Adsorbents may give off flammable or toxic material, and in some cases ignite spontaneously in the presence of air.

The other type of solid is residues in the form of deposits and sludges. These also may be flammable or toxic. It is generally necessary to remove these by cleaning, although for certain activities there may be alternative sale methods of working, as described below.

A particular pyrophoric material often encountered in refinery processes is iron sulphide. If dry, this will burst into flames on contact with air, but if wet it is harmless. It may be dealt with by injecting inert gas and soaking the iron sulphide with water.

Oil soaked lagging, removed whilst it is still hot, can behave like a pyrophoric material and burst into flames on contact with air.

21.3.8 Cleaning

There are a number of methods available for cleaning. The choice of method of cleaning depends on the type of plant, on its initial contents, including residues, and on the work to be done. The methods are described in Section 21.6.

21.4 Isolation

As already described, much maintenance work is subject to potential hazards from noxious materials, energy sources, rotating equipment and electrical power. Where work is to be done, the necessary isolations should be made to ensure that it can be done safely. Accounts of isolation are given in the IP *Refining Safety Code,* the IP *LPG Code*, the OIAC *Permit Systems Code,* the IChemE *Maintenance Guide* and by Kletz (1982f).

Isolation may be required prior to installation, inspection, servicing, repair, cleaning or dismantling. Where a job involves isolation of equipment, there should be separate permits-to-work for the three phases: (1) isolation, (2) main job and (3) de-isolation. Permit systems are described in Section 21.8.

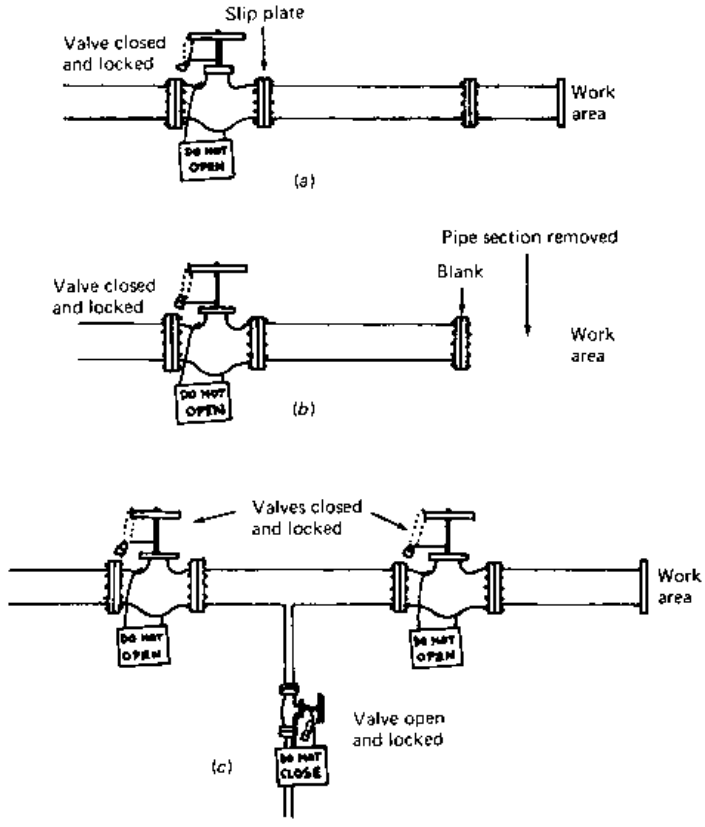


Figure 21.1 *Some methods of isolation of pipework – 1: (a) locked valve with slip plate; (b) locked valve with blank and with section removed; (c) locked double block and bleed valves*

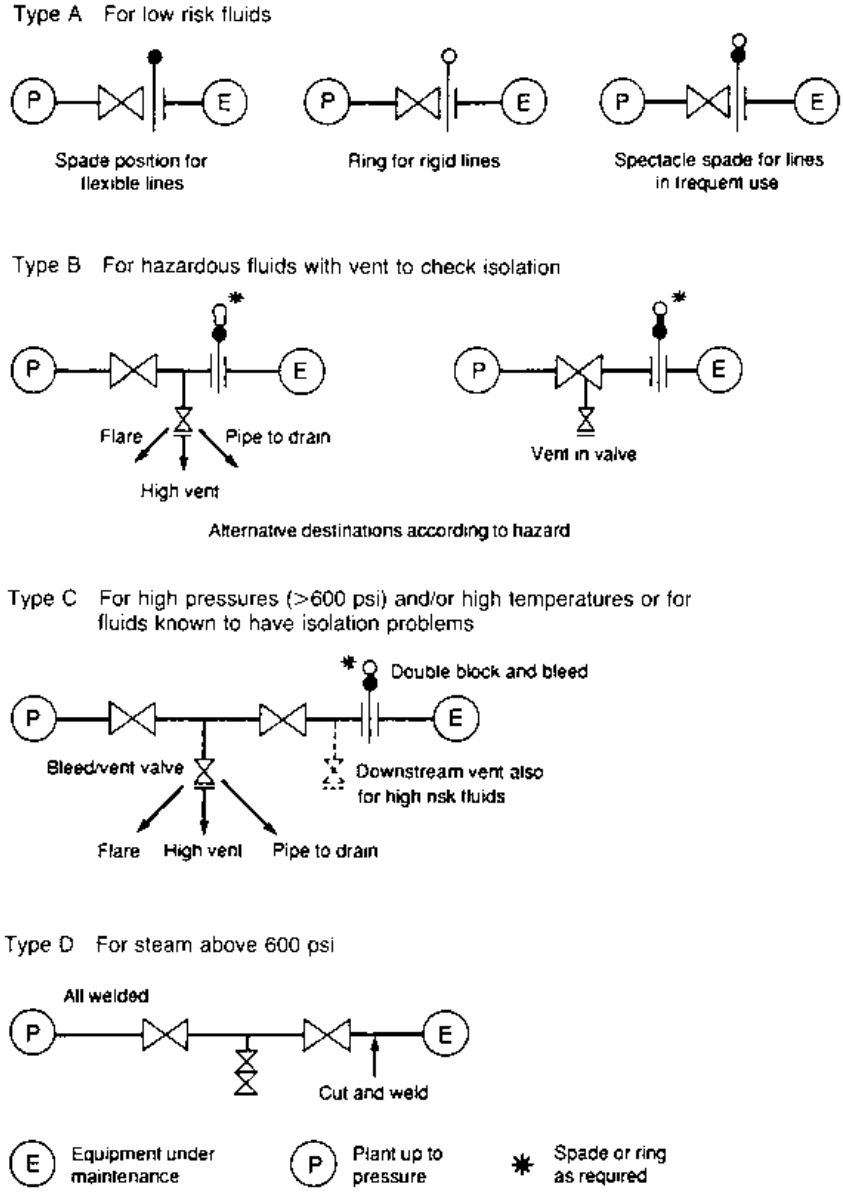


Figure 21.2 *Some methods of isolation of pipework – 2 (Townsend, 1992) (Courtesy of the Institution of Chemical Engineers)*

21.4.1 Isolation of vessels and pipes

The methods available for isolating a vessel or pipe are, in ascending order of effectiveness, the use of (1) a closed and locked valve, or valves, (2) a double block and bleed valve system, (3) a slip plate and (4) physical disconnection.

The least effective of these methods of isolation is the use of a closed and locked isolation valve. There have been numerous incidents in which either the valve has corroded or jammed and has passed fluid or it has been opened in error. Even two isolation valves in series do not always prevent the passage of fluid.

More positive isolation is obtained by the use of a double block and bleed valve system as shown in Figure 21.1(c). The two block valves are closed, the bleed valve is open and all three are locked. If the fluid passes

though the first block valve, it is vented by the bleed valve so that no pressure should build up which would allow the material to pass through the second block valve. A build-up of pressure can occur if the bleed line is too small or too long, or if it discharges into a vent system in which there may be a back pressure.

As shown in Figure 21.1(a), isolation may be effected by the insertion into the line of a slip plate, also called a blind or spade. In the system shown, the valve is first closed and locked and the slip plate is then inserted. If a slip ring or spectacle plate is installed, it may be used instead of a slip plate.

The most positive method of all, shown in Figure 21.1(b), is complete physical disconnection of the line, with a blind flange, or blank, put on the 'live' line.

Where isolation is by means of a closed valve, this should be an isolation valve rather than a control valve, unless the latter can be tightly shut, disconnected from any power source, locked in the closed position and the isolation tested as being effective.

Isolation valves should be locked and tagged. The preferred arrangement is a valve which can be locked with a captive key system or which has lugs for padlocking. The alternative is the use of a padlock and chain. A warning notice should be securely attached to the valve, stating whether it is locked in the open or closed position and prohibiting unauthorized movement of it, and showing the equipment identification number, the isolation lock number and the isolation permit number.

On systems containing hazardous fluids such as hydrocarbons under pressure, the arrangements for closing off the end of a line with a blind flange should ensure that the joint is leak tight. The fixed flange and the blind flange should be inspected for deterioration, a ring-joint blank should be fitted with a new ring, and the bolts should be properly tightened.

The slip plates and blind flanges used should be strong enough to withstand the highest pressure which may occur in the main if the shut-off valves are opened accidentally. Slip plates should be used only for low pressure isolation. Each slip plate should have an identification tag.

With regard to the choice of isolation arrangement, where there is to be work on a pressurized hydrocarbon system or entry into a vessel, physical disconnection is the only recommended method of isolation. If this method is not reasonably practicable, the next best method is the insertion of a slip plate or of a slip ring or spectacle plate.

The closed and locked isolation valve method should be used only for the isolation of low hazard fluids. Another principal use is to effect preliminary isolation whilst a slip plate is inserted.

The double block and bleed system is more effective than a closed isolation valve and is used for more hazardous fluids. It does not, however, provide adequate isolation for long periods. This method also finds a principal use in effecting preliminary isolation whilst a slip plate is inserted.

Figure 21.2 shows the methods of isolation given in the IChemE *Maintenance Guide*. In addition, there are certain preferred arrangements for isolation in specific cases. For entry into a vessel or confined space, isolation should be by physical disconnection.

For the isolation of relief valves and vent lines, physical disconnection is again the preferred method. Where this is not possible, the relief valve or vent line should be blinded off first and deblinded last.

The need should be considered for isolation of drains and sewers through which hazardous materials may spread to other sections of the plant.

The plant should be designed to facilitate isolation, particularly at points where isolations are likely to be frequent. A pressure gauge and drain point can be provided downstream of an isolation valve which is used to provide preliminary isolation for the insertion of a slip plate. A double block and bleed valve system can be installed to provide more positive isolation for the same purpose. Slip rings and spectacle plates can be provided. All critical valves should be identified with a permanent marking.

There should be a system for the identification and control of slip plates and blind flanges for different duties. The system should ensure that slip plates are correctly identified and that they do not become mixed up. It should also ensure that slip plates are neither left in when they should be taken out nor left out when they should be inserted. For equipments where a number of slip plates need to be inserted for isolation, it is helpful to have a list of slip plates and a diagram showing the insertion points.

21.4.2 Isolation of machinery

Where work is to be done on powered machinery, the source of power should first be isolated. Sources of power include electrical, hydraulic and pneumatic power, and engines.

A hydraulic or pneumatic supply should be isolated as follows. First preliminary isolation should be effected by closing a valve. Then the supply and return pipes should be disconnected, or otherwise made safe. The isolation of electrical supplies is described below.

Isolation of an engine-driven system should be done by shutting off the engine fuel supply and then isolating and disconnecting all starting systems.

It may sometimes be possible for the machinery to move even though it is disconnected from its power source, and in such cases it should be secured to prevent such movement.

A system of warning notices should be used based on principles similar to that for the isolation of plant.

21.4.3 Isolation of electrical equipment

Electrical isolation may be required either to immobilize machinery or to protect personnel working on electrical equipment.

Situations involving electrical isolation include work on powered equipment, including rotating machinery and machinery with moving parts, and entry into vessels which contain stirrers or agitators.

Where isolation of fluids is required, electrical isolation should be a complement to, but not a substitute for, mechanical isolation.

The isolation of electrical equipment is governed by the Electricity at Work Regulations 1989 and advice is given in the associated *Memorandum of Guidance* (HSE, 1989 HS(R) 25). Electrical isolation should be performed only by an electrically competent person.

Two methods of effecting the electrical isolation of equipment are to withdraw the fuses and to lock off the isolator. There is evidently some difference of view on the merits of the two methods. Some authorities describe systems based primarily on isolator lock-off. The IChemE *Maintenance Guide* describes fuse withdrawal as suitable where isolator lock-off is not available, as with instruments, heaters, lighting circuits. Anon. (1983 LPB 49, p. 7) argues that a fuse is always liable to be replaced. On the other hand, Kletz (1982f) states that experience has shown that isolator lock-off is not always effective. He recommends fuse withdrawal where the work to be done is on electrical circuitry.

A system of electrical isolation based on isolator lock-off is described by Anon. (1983 LPB 49, p. 7). A lock-off device is a mechanism or arrangement which allows the use of key operated padlocks to hold a switch lever or handle in the 'off' position. The lock-out procedure is to switch off, lock off and confirm lock-off by checking that the equipment will not restart. The lock-off should be applied to the isolator switch itself and not to some remote stop/start button. Where there is more than one power source, all should be locked off.

The lock-off system described by this author is as follows. For operations, each padlock should be issued through the operations foreman and should be capable of being opened only by the one key issued with it. There should be a lock-off log in which should be recorded the identification of the locked-off equipment, the date and time of application of the padlock and the operator applying it, and the date and time of its removal and the operator removing it.

The maintenance craftsman applies his own lock to the isolator before starting work and removes it when he is finished. Where the equipment is to be worked on by several crafts, each craftsman applies this procedure. If a shift change occurs, the outgoing craftsman removes his lock and the relieving one applies his own lock. When the job is complete, the last lock to be removed is that of the operator.

With regard to the isolation of electrical systems, to protect personnel working on or near them, guidance is given in the relevant British Standards. Switchgear and controlgear are covered by BS 5486: 1988– (low voltage), BS 6423: 1983 ($V \leq 1$ kV), BS 6626: 1985 (1 kV $< V \leq 36$ kV) and BS 6867: 1987 ($V > 36$ kV).

All items of electrical equipment should have permanent labels, and their separate parts should be identifiable. For a prime mover the IChemE *Guide* gives these as the drive unit, the isolator/connector and the stop/start button. A system of warning notices should be used.

21.5 Purging

Purging involves replacing one gas or vapour with another. It is performed for a variety of purposes and using a number of different purging media. Guidance on purging is given in *Purging Principles and Practice* (AGA, 1975) (the AGA *Purging Guide*). Further accounts of purging are given in the IP *Refining Safety Code,* CS 15 (HSE, 1985), the IP *LPG Code,* the IChemE *Maintenance Guide,* and by Kletz (1982f).

Purging may be used to take a unit out of service by replacing flammable or toxic process gas with an inert medium and then with air. It may be used to bring a unit back into service by replacing air with an inert medium and then with the process gas.

The AGA *Purging Guide* gives purging end-points for a number of different cases. The end-point data cover two purge gases: nitrogen and carbon dioxide. Values are quoted for the concentration which will just render a mixture non-flammable and for that which allows a 20% 'safety factor'. Selected purge end-points taken from the guide, are shown in Table 21.2. Section A gives inert gas end-points for purging into service (i.e. purging air out of a system subsequently to be filled with flammable gas), together with an alternative set of oxygen end-points which may be more convenient to use. Section B of the table gives inert gas end-points for purging out of service (i.e. purging flammable gas out of a system subsequently to be filled with air), together with an alternative, and often more convenient, set of combustible gas end-points. The values given without brackets are the concentrations required to just render the mixture non-flammable, whilst those in brackets give the 20% safety factor.

Further details of the purging of tanks prior to entry or hot work, including sources of purge gas, purge end-points and precautions, are given in Section 21.12. The purging of refinery units is described in Chapter 20.

Table 21.2 *Selected end-points for purging (after American Gas Association, 1975)*

A Inert gas and oxygen end-points for purging into service

Gas	*Concentration of gas to render mixture non-flammable* (% v/v)[a]	
	Nitrogen	*Oxygen*
Hydrogen	71 (77)	5.0 (4.0)
Methane	36 (49)	12.1 (9.7)
Propane	42 (54)	11.4 (9.1)
Butane	40 (52)	12.1 (9.7)
Ethylene	49 (59)	10.0 (8.0)
Propylene	42 (54)	11.5 (9.2)

B Inert gas and combustible gas end-points for purging out of service

Gas	*Concentration of gas to render mixture non-flammable* (% v/v)[a]	
	Nitrogen	*Combustible gas*
Hydrogen	95 (96)	5 (4)
Methane	86 (89)	14 (11)
Propane	94 (95)	6 (5)
Butane	95 (96)	5 (4)
Ethylene	94 (95)	6 (5)
Propylene	96 (97)	4 (3)

[a] Values without brackets are the concentrations to just render the mixture non-flammable, those in brackets are the concentrations which give a 20% safety factor.

21.6 Cleaning

There is a wide variety of methods of cleaning plant. They include (1) water washing, (2) chemical cleaning, (3) steaming, (4) water jetting, (5) solvent jetting, (6) shot blasting and (7) manual cleaning.

The choice of cleaning method depends on the type of plant and on the nature of the material to be cleaned out. Most of these methods are described in CS 15 and/or the IChemE *Maintenance Guide.*

Some methods of cleaning are now described. Further details of cleaning of tanks prior to entry or hot work are given in Section 21.12.

21.6.1 Water washing

In some instances adequate cleaning may be obtained by flushing with water. In most cases, however, something more is required.

Washing with cold water, or even purging with air, have sometimes been used in an attempt to remove oil, but these are generally not effective methods for this purpose and reliance on them has been the cause of many accidents.

Another process, also referred to as water washing, comprises immersion of the article in a boiling aqueous caustic or detergent solution. This may be used for small tanks which can be completely immersed. It is necessary to select the cleaning agent so as to avoid chemical attack, to exclude air and to boil for at least 30 minutes.

Another form of water washing is the use of a high pressure jet of hot detergent solution directed onto the interior surfaces. This latter method is used in combination with steaming to clean drums.

21.6.2 Chemical cleaning

Tanks may be cleaned by chemical cleaning using special chemicals. This is a specialized operation. The precautions to be taken are given in the IChemE *Maintenance Guide.*

21.6.3 Steaming

Steam cleaning is used particularly for fixed and mobile tanks. It is convenient to describe it in relation to tanks of different sizes as given in CS 15.

The procedures given in CS 15 for the steaming of small tanks ($< 60\,m^3$) are broadly as follows. Steam is admitted to the tank, taking care that no excess pressure develops which could damage it. Condensate should be drained from the lowest possible point, taking with it the residues. The temperature reached by the tank walls should be sufficient to ensure removal of the residues, a steam pressure of 2 barg generally being sufficient, and the tank should be held at this temperature for a minimum of 30 minutes. The progress of the cleaning may be monitored by the oil content of the condensate.

CS 15 gives a number of precautions to minimize the risk from static electricity. There should be no insulated conductors inside the tank. The steam hose and tank should be bonded together and well earthed; it is desirable that the steam nozzle have its own separate earth. The nozzle should be blown clear of water droplets prior to use. The steam used should be dry as it leaves the nozzle; wet steam should not be used, as it can generate static electricity even in small tanks, but high superheat should also be avoided, as it may damage equipment and even cause ignition. The velocity of the steam should initially be low, though it may be increased as the air in the tank is displaced. Personnel should wear conducting footwear.

Consideration should be given to other effects of steaming. One is the thermal expansion of the tank which may put stress on associated pipework. Another is the vacuum that occurs when the tank cools again. Tank openings should be sufficient to prevent the development of a damaging vacuum.

Mobile tanks on road tankers and rail tank cars may be cleaned by steaming in a similar manner. Steaming may also be used for large tanks, but in this case the supplies of steam required can be very large. There is also the hazard of static electricity, and in some companies it is policy for this reason not to permit steam cleaning of large storage tanks which have contained volatile flammable liquids.

21.6.4 Water jetting

Another method of cleaning is high pressure water jetting. A high pressure water jet can cut through most metals and polymers and can clean a surface of paint or deposits. Accounts of water jetting are given by Donaldson (1986) and Jacob (1990). The relevant code is *Code of Practice for the Use of High Pressure Water Jetting Equipment* (High Pressure Water Jetting Contractors, 1982).

The technique is widely used by civil engineers for a variety of purposes, varying from the cleaning of buildings, roads and drains to the removal of spalled concrete. It is now being increasingly used in the process industries. One application is the removal of deposits from equipment such as heat exchangers and tanks. Another is the cutting of metal, which is exploited for the cutting up of tanks and pipework during demolition.

In water jetting the jet is held quite close to the surface, about 75–100 mm. A water jet can remove material from a surface if the energy transferred per unit area exceeds a threshold value which is characteristic of the material. Since the energy is a function of the jet velocity and this in turn is a function of the pressure, this threshold energy can be specified in terms of the nozzle pressure for typical practical flows. The pressures used in water jetting have risen from about 200 bar through 1000 bar and are now up to 2000 bar. Some threshold cutting pressures given by Jacob are: 200 bar for soft wood; 800 bar for concrete; and 2000 bar for aluminium or paint, although aluminium can be damaged at a pressure of 200 bar.

A 2000 bar jet may operate with a flow as low as 10 l/min. At this flow the reaction force is of the order of 15 kg_f, which is manageable for an operator. Jacob gives a maximum recommended value of 25 kg_f and states that at 30–40 kg_f an operator struggles to keep control. The cutting rate is controlled by adjusting the flow rather than the nozzle pressure and any increase in flow results in an increase in reaction force. One hazard of water jetting is thus loss of control of the jet.

Another potential hazard is the aerosol produced, which can be harmful, depending on the material involved. The use of protective clothing is necessary.

In addition to manual cleaning operations, water jetting is used in fixed systems for cleaning tanks and vessels. A typical arrangement is a set of four jets set at right angles to each other on the same plane and mounted on a head which itself rotates to give coverage in all directions. In such tank cleaning applications the travel distance for the jets is much greater, and their removing power correspondingly less.

CS 15 gives water jetting as a suitable method for the cleaning of large tanks, but draws attention to the static electricity hazard.

21.6.5 Solvent jetting

Another method used for drum cleaning is high pressure solvent jetting, with recirculation of the solvent. The method is promoted for difficult residues. The solvents used are flammable and create a flammable atmosphere inside the drum. It is necessary to take precautions against static electricity and to undertake gas freeing afterwards.

According to CS 15, the process must be regarded as more hazardous for drum sizes greater than the standard size of 200 l, partly because of the larger volume and partly because of lack of information on the static electricity risk.

21.6.6 Shot blasting

A quite different method of cleaning is the use of shot blasting, or grit blasting. In this method a stream of fine abrasive particles is directed at the surface to be cleaned in a jet of air. The method is widely used for cleaning surfaces, particularly for painting. Precautions to be taken in shot blasting are given in the IChemE *Maintenance Guide*.

21.6.7 Manual cleaning

In some cases it is necessary to resort to manual cleaning. This method may have to be used, for example, where a tank contains residues which are difficult to shift in any other way but which must be removed. A typical case is the removal of flammable residues in a large tank in preparation for hot work. Manual cleaning is generally a last resort; it is laborious and unpleasant, and requires full precautions against flammable, toxic and asphyxiation hazards.

21.6.8 Cleaning in place

A method of cleaning which is now a standard one in the pharmaceutical, as well as the food industry, is cleaning in place, using detergents. Accounts are given by Hyde (1985) and Kirkland (1986).

Cleaning in place (CIP) systems offer a number of advantages. They minimize downtime by more rapid cleaning and generate less effluent, and can be less costly. They minimize manual operations and hence both safety and health problems. In particular, hazards of vessel entry and slippery surfaces are reduced.

CIP systems come both as systems dedicated to particular units and as mobile systems which can be used on a number of units. They may operate under manual control or under automatic control, with a programmed sequence.

The equipment to be cleaned may be closed or open. For open equipment, Kirkland describes the use of a sprayball custom-designed by computer, for the particular vessel.

A typical CIP sequence is: (1) a water pre-rinse, to remove gross material; (2) detergent circulation, to remove debris and scale; (3) an intermediate water rinse, to remove detergent; (4) sterilant circulation, to destroy residual organisms; and (5) a final water rinse, to remove CIP solutions.

There are various techniques for water recovery and for minimizing the quantity of solutions used.

21.6.9 Line clearing

It is often necessary to remove debris, as distinct from shifting a complete blockage, from a line by flushing with water or blowing it with air.

A treatment of the effectiveness of this operation has been given by Junique (1988). This is based on the following simple model of flushing or blowing:

$$F \propto \rho u^2 \qquad [21.6.1]$$

where F is the drag force on the particle, u is the fluid velocity relative to the particle and ρ is the density of the fluid. He defines a cleaning disturbance factor such that

$$C = \frac{\rho_1 u_1^2}{\rho_2 u_2^2} \qquad [21.6.2]$$

where C is the cleaning disturbance factor and subscripts 1 and 2 denote cleaning and operating conditions, respectively. The condition for effective flushing or blowing is $C > 1$.

The author gives an example of the application of the method.

21.6.10 Waste minimization

Cleaning operations generate an appreciable fraction of the liquid effluents from process plants and measures to reduce effluents from this source can contribute significantly to waste minimization. This aspect is considered in Appendix 11.

21.7 Confined Spaces

Accidents associated with entry into and work in confined spaces and vessels have recurred with depressing regularity. The activity is recognized as presenting particular potential hazards and is governed by a statutory requirement for a permit-to-work. Permits as such are considered in Section 21.8. The account given here is confined to the hazards of confined spaces and to precautions which should be taken. Accounts of these hazards and precautions are given in the IChemE *Maintenance Guide*, in a series of articles in the *Loss Prevention Bulletin* (Anon., 1975 LPB 3, p. 8; Anon., 1980 LPB 31, p. 11; Anon., 1983 LPB 53, p. 15; Anon., 1984 LPB 56, p. 24; Anon., 1985 LPB 63, p. 31), in the work of Kletz (notably Kletz, 1982f, 1985b), and by Arney (1977a,b), Bond (1984 LPB 59), Keller (1987) and Trowbridge (1987).

Early HSE guidance on confined spaces is that given in TDN 45 *Entry into Confined Spaces: Hazards and Precautions* (HSE, 1975) and GS 5 *Entry into Confined Spaces* (HSE, 1977) with current guidance being given in Construction Sheet 15 *Confined Spaces* (HSE, 1991).

21.7.1 Confined spaces

In some cases it is fairly obvious what constitutes a 'confined space', in others it is less so. The HSE (1991 Construction Sheet 15) defines a confined space in the following terms:

> A closed tank with restricted access may be the obvious example of a confined space, but it also includes open manholes, trenches, pipes, flues, ducts, ceiling voids, enclosed rooms such as basements, and other places where there is inadequate natural ventilation.

Open top tanks, furnaces and ovens, even those with a large aperture open to the atmosphere, are confined spaces.

A classification of confined spaces is given by Anon. (1983 LPB 53, p. 15) as follows:

Class A Confined space which has contained a flammable or explosive gas or dust, or asphyxiating material, and where there may be a hazardous concentration or residue.

Class B Confined space which has contained a flammable, explosive or asphyxiating gas or dust, but where there is no hazardous concentration or residue.

Class C Confined space which has contained acidic or alkaline chemicals.

Class D Confined space which has vertical or maze exit.

Class E Confined space which contains loose dust, fluidized materials, or unstable solids.

21.7.2 Flammable substances

It is frequently necessary for personnel to enter a tank or vessel which has contained flammable materials. Before this is done it is obviously necessary to empty the tank and to purge and clean it so that flammable materials are no longer present. However, despite this incidents recur in which a flammable atmosphere builds up and is ignited. Other incidents occur in which the flammable residues are ignited when hot work is done.

If a flammable mixture is ignited inside a tank or vessel, the resultant explosion is likely to destroy it, since even pressure vessels are not generally designed to withstand an explosion. Unburned and burned gases and burning liquid may be expelled and missiles generated from the disintegration of the tank.

There are several situations which can lead to the existence of a flammable atmosphere in the tank. One is simply that flammable vapour which was originally present has not been completely removed. Another is that flammable residues remain in the tank and evaporate. In some cases the residues are trapped in construction members in the tank. In other cases they may be solid residues which vaporize when heat is applied such as from welding. Another way in which flammable gases may build up again is through isolations which are not leak-tight. In particular, the use of a single closed isolation valve is an unreliable means of isolation and there have been many instances where flammable fluid has entered a tank through a passing isolation valve. A fourth way is the generation of a flammable gas by chemical reactions, e.g. the action of water on steel can generate hydrogen.

Liquid residues should be drained out by drilling appropriate holes, whilst solid residues should be removed by cleaning. In-leak of flammable fluids should be prevented by positive isolation, as described in Section 21.4.

Prior to entry into a tank a gas test should be done to confirm that the space is free of flammable gas. In some incidents there has been a failure to free the tank completely of flammable gas and to test for this. More commonly, however, incidents occur because flammable gas builds up in the tank atmosphere after it has been checked and found to be free of flammables.

Even if gas tests show the tank atmosphere to be essentially free of flammables, however, there may still be flammable residues or deposits which can be ignited by hot work. It is necessary, therefore, to check separately for these and to clean them away before hot work is undertaken.

21.7.3 Toxic substances

There is a parallel hazard with toxic substances. The precautions taken to ensure that the tank atmosphere is free of toxic gas are essentially similar to those taken from flammable substances. The tank is emptied, purged, cleaned and tested for the relevant toxic gases. But a toxic atmosphere may still arise from residues remaining in the tank or from leaks through inadequate isolation.

21.7.4 Oxygen-deficient atmospheres

The removal of flammable gas from a tank is often effected by purging with nitrogen. This inert gas is then replaced with air by purging or ventilation so as to give a breathable atmosphere. Incidents occur in which workers are asphyxiated because the atmosphere is deficient in oxygen.

An oxygen-deficient atmosphere may arise in several ways. The original purging or ventilation may be inadequate. Alternatively, the purge may have been conducted inadvertently using nitrogen instead of air. One way in which such inadvertent use of nitrogen in place of air may occur is where the air line has been connected to a nitrogen supply line. Another is the use of a cylinder which is supposed to contain air, but contains some other mixture.

An atmosphere can also be rendered oxygen deficient if there is some process occurring which consumes the oxygen present, such as the rotting of vegetation or the rusting of metal. Oxygen may be adsorbed on steel surfaces, especially where these are damp.

Where the hazard of an oxygen-deficient atmosphere exists, a test of the oxygen content should be done.

Requirements for the oxygen content of breathable air vary. The oxygen content of air at sea level is 21%, but at high altitudes it can fall to 19.5%. The concentration usually quoted to sustain life is 16%. Some standards or codes require for breathable air an oxygen content of 21%, others one of 19.5% or 19%. In relation to tank atmospheres CS 15 quotes a minimum oxygen concentration of 19%.

21.7.5 Oxygen-enriched atmospheres

In some cases an oxygen-enriched atmosphere may occur in a confined space. Such an atmosphere is hazardous because it can enhance strongly the flammability of clothing.

One way in which the atmosphere may become oxygen rich is by leakage of oxygen from an oxygen cylinder used in cutting or welding operations such as oxypropane cutting.

Another way is where the atmosphere is originally a mixture of nitrogen and oxygen which is nitrogen rich compared with air and where oxygen has been added in an attempt to raise the concentration to that present in air. This is poor practice precisely because it involves this hazard.

21.7.6 Noxious fumes

There are a number of other ways in which noxious fames may enter a confined space. One is from processes being carried out in that space. A common source is the fumes arising from welding. Another source is an adjoining space which has not been isolated. Other sources of noxious fumes are sludges and residues and combustion products.

Trenches, tunnels and manholes in chalk soil can fill with carbon dioxide. Other fumes may occur where the ground is contaminated. Where these spaces are connected even temporarily to sewers, the atmosphere may become contaminated with flammable and/or toxic gases or rendered oxygen deficient.

21.7.7 Gas tests

As already described, prior to entry into a tank it should be confirmed by such gas tests as are necessary that the atmosphere is free of flammables and toxins and that it is breathable. The gas tests which are commonly done are for hydrocarbons, carbon monoxide and hydrogen sulphide, and oxygen, together with tests for any toxic substance which has been contained in the tank.

21.7.8 Air supplies

Measures to ensure that nitrogen is not supplied when it is intended to supply air to render an atmosphere breathable are described by Anon. (1975 LPB 3, p. 8). Incidents have occurred where an air line has been connected to a nitrogen supply, a nitrogen cylinder has been used instead of an air cylinder, and where an air cylinder has contained an oxygen deficient mixture.

There are certain precautions which may be taken to ensure that an air line is not connected in error to a nitrogen supply line. One is to put an identification sign at each nitrogen take-off point. A more positive measure is to ensure that the connections for nitrogen and air lines are different and that their designs are such as to prevent an air line being connected to a nitrogen line.

Measures should also be taken to ensure that where air is to be supplied from a cylinder, the gas obtained actually is air. A positive means of preventing inadvertent use of a nitrogen instead of an air cylinder is the provision of different connections on the two types of cylinder, though this is outside the authority of the user company. Otherwise, procedures should be established to avoid identification errors.

Cylinders of breathable air should be analysed at a frequency that is sufficient to ensure the contents meet the specifications.

It is preferable not to use reconstituted air, made by blending nitrogen, oxygen and other gases, for breathing purposes, but if this is done each cylinder should be analysed.

21.7.9 Entry into confined spaces

It will be apparent that entry into a confined space or vessel needs to be governed by procedures which ensure that the hazards are identified and precautions taken. This is effected by the permit-to-work system, which is now considered. Entry procedures are a prime example of the application of a permit system.

21.8 Permit Systems

Maintenance work on process plants should be controlled by a formal system of permits-to-work (PTWs). Accounts of such systems are given in *Permit-to-Work Systems* (CAPITB, 1977 Inf. Pap. 16A), *Guidance on Permit-to-Work Systems in the Petroleum Industry* (OIAC, 1991) (the OIAC *Permit Systems Guide*) and the IchemE *Maintenance Guide,* and by Kletz (1982f), V.C. Marshall (1986b), S. Scott (1992) and Butler and Bonsall (1993).

21.8.1 Regulatory requirements

In the UK there has long been a statutory requirement for a pennit system for entry into vessels or confined spaces under the Chemical Works Regulations 1922, Regulation 7. Although these regulations have recently been superseded, they have given this permit requirement a rather special status, as described below. There is no exactly comparable statutory requirement for other activities such as line breaking or welding.

The Factories Act 1961, Section 30, which applies more widely, also contains a requirement for certification of entry into vessels and confined spaces. Other sections of the Act which may be relevant in this context are Sections 18, 31 and 34, which deal, respectively, with dangerous substances, hot work and entry to boilers.

The requirements of the Health and Safety at Work etc. Act 1974 to provide safe systems of work are also highly relevant. In many cases a permit-to-work system is the appropriate solution.

21.8.2 Objectives of permit system

In essence, the objectives of the permit system are to exercise control over the maintenance activities by assigning responsibilities, ensuring communication between interested functions, and requiring that proper consideration be given to the job, its hazards and the precautions required.

More explicitly, the objectives are to ensure that:

(1) there is a system of continuous control of the work to be done;
(2) the persons responsible for overall control of the work and for its execution are identified;
(3) the person responsible for the operation of the plant is aware of the work;
(4) the other functions with an interest in the work are identified and communications with them are established and maintained;
(5) the work is properly defined;
(6) the work is properly authorized by the person responsible;
(7) the person responsible for the operation of the plant is aware of what is going on;
(8) the personnel involved in doing the work understand its exact nature and extent, the hazards involved, any

limitations on the extent, and the time allotted for the work;
(9) the isolations and de-isolations required are properly effected;
(10) the precautions to be taken are specified and understood;
(11) the equipment is available and the arrangements are in place to support these precautions;
(12) there is cross-referencing of permits where there is interaction between jobs;
(13) the permits are suitably displayed;
(14) there is a formal handover procedure from operations to maintenance;
(15) there is a formal handback procedure from maintenance to operations;
(16) there is a procedure covering situations where the work extends beyond a single shift;
(17) there is a procedure covering situations where the work has to be suspended;
(18) there is a record showing that the nature of the work and the precautions necessary were checked by the appropriate person(s).

21.8.3 Issuing and performing authorities

It is a principal objective of the permit system to define the responsibilities of all concerned. In the normal system there is an issuing authority and a performing authority. The issuing authority is the operations supervisor. The performing authority is usually the maintenance craftsman who is to do the work, but may sometimes be the maintenance supervisor.

It is the responsibility of the issuing authority to ensure that the plant is safe for the work to proceed. The performing authority is responsible for ensuring that the further working precautions are taken. In certain cases, such as maintenance work on switchgear, the operations supervisor is not competent to give clearance, and so the maintenance supervisor has a greater degree of responsibility than usual.

It is the responsibility of these same two authorities to terminate the permit. The normal system is that on completion of the work the performing authority signs that the work is complete and the issuing authority, after inspecting the work site, signs that the permit is cancelled.

There may be a requirement that in certain defined cases where work at a particular plant may affect an adjacent plant, the operations supervisor on the latter should countersign the permit.

21.8.4 Types of permit

There is a variety of types of permit, some of which have special names, e.g. clearance certificates, fire permits, etc. Permits may be classified by reference to the operation to be performed, the equipment to be worked on, the classification of the areas where the work is to be done, the special hazards which may be encountered, the equipment to be used or the time of day specified for the work. A list of typical permits, which illustrates all these categories, is as follows:

Operations
Equipment removal
Excavation
Hot work
Leak sealing
Line breaking
Vessel entry
Waste disposal

Equipment worked on
Electrical equipment
Interplant pipelines
Sprinkler system

Area classification
Flammable area

Special hazards
Corrosive substances
Fire
Toxic substances
Ionizing radiations

Equipment used
Mobile crane

Time of day
After-hours work

A common basic set of permits covers entry, cold work, hot work and electrical work. The IP *Refining Safety Code* gives model permit forms for the following: general work, electrical work, hot work and work involving ionizing radiations; line disconnecting and vessel opening; entry; and excavation.

21.8.5 Permits for isolation

Isolation before a job and de-isolation after it should be treated as separate activities in their own right and governed by separate permits. Thus for a job which requires isolation there should be permits for (1) isolation, (2) the main job, and (3) de-isolation.

Permit 2 should not be issued until isolation has been effected, permit 1 has been handed back and the responsible person has checked that the isolation is complete. A similar approach should apply to permit 3.

21.8.6 Contents of permit

The contents of a permit need to be carefully defined. Accounts of permit contents are given in the OIAC *Permit Systems Guide,* the IChemE *Maintenance Guide* and by S. Scott (1992). Such accounts usually distinguish between features which are essential and those which are desirable.

The essential features of a permit are:

(1) company name and address;
(2) permit title;
(3) permit number;
(4) period of validity;
(5) location of work (plant, equipment);
(6) description of work;
(7) isolation;
(8) hazard identification;
(9) precautions required;
(10) protective equipment required;
(11) authorization;
(12) extension;
(13) handback;
(14) cancellation.

The period of validity, in terms of the date, start time and end time, should be entered, as an elementary requirement for control. The location of the work should be specified in terms of the plant, plant area or building and vessel or equipment. Proper titles should be used, not informal names. The equipment may be identified by an identification tag and this should be cross-referenced on the permit. The description of the work should state the work to be done, the reason for it and the method to be used, and any limitations on the extent of the work. There should be confirmation that the isolation required has been effected. The potential hazards should be identified. In some cases these may be partially covered by a checklist of actions to be taken such as depressurization, cleaning, etc., in which case it is the residual hazards which are entered. The precautions already taken and those still to be taken should be stated. The protective clothing and equipment to be used should be specified. The issuing authority should sign that the work is authorized to start and the performing authority should sign that the permit is accepted. On completion, the performing authority should sign to indicate that the work is complete and the issuing authority should sign to show that the permit is cancelled.

Particular types of permit require additional features. For example, a hot work permit should contain an entry for the hazardous area classification of the location of the work.

The IChemE *Maintenance Guide* gives a number of additional desirable features. It is desirable to include a caution to the effect that the permit is a legal document; a caution to the issuing authority that, although work may be delegated, responsibility remains with him; an indication of the levels of hazard, so that high hazard situations are highlighted and those involved are prompted to consider whether there are other parties who should be consulted; an indication of work progress, so that cases are identified where the work is tending to expand beyond that originally envisaged and those involved are prompted to reappraise it.

21.8.7 Design of permit forms

Sample permit forms are given in a number of publications, including the IP *Refining Safety Code,* the IP *LPG Code* and the IChemE *Maintenance Guide.*

A typical permit-to-work, referred to by the company concerned as a clearance certificate, is shown in Figure 21.3. This permit dates from 1977, but still provides a clear illustration of many of the basic principles.

Figure 21.4 shows the typical entry permit given in the IChemE *Maintenance Guide.*

21.8.8 Entry permits

Entry into vessels and other confined spaces has resulted in numerous accidents. As a result this operation has had a unique status. It is the only one where there has been a specific legal requirement for a permit system. This requirement is given in the Chemical Works Regulations 1922, Regulation 7, now superseded, and in the Factories Act, Section 30. It is appropriate, therefore, to describe this permit in some detail as an illustration. In order to avoid repetition it is also convenient to describe here the associated hazards and procedures.

Entry permits are dealt with in *Safety and Management* (ABCM, 1964/3), *Permit-to-Work Systems* (CAPITB, 1977 Inf. Pap. 16A) and by Kletz (1982f). Early HSE guidance was given in TDN 47 *Entry into Confined Spaces: Hazards and Precautions* (HSE, 1975) and GS 5 *Entry into Confined Spaces* (HSE, 1977) and current guidance in Construction Sheet 15 *Confined Spaces* (HSE, 1991). The hazards of work in a vessel or confined space are described in Section 21.7.

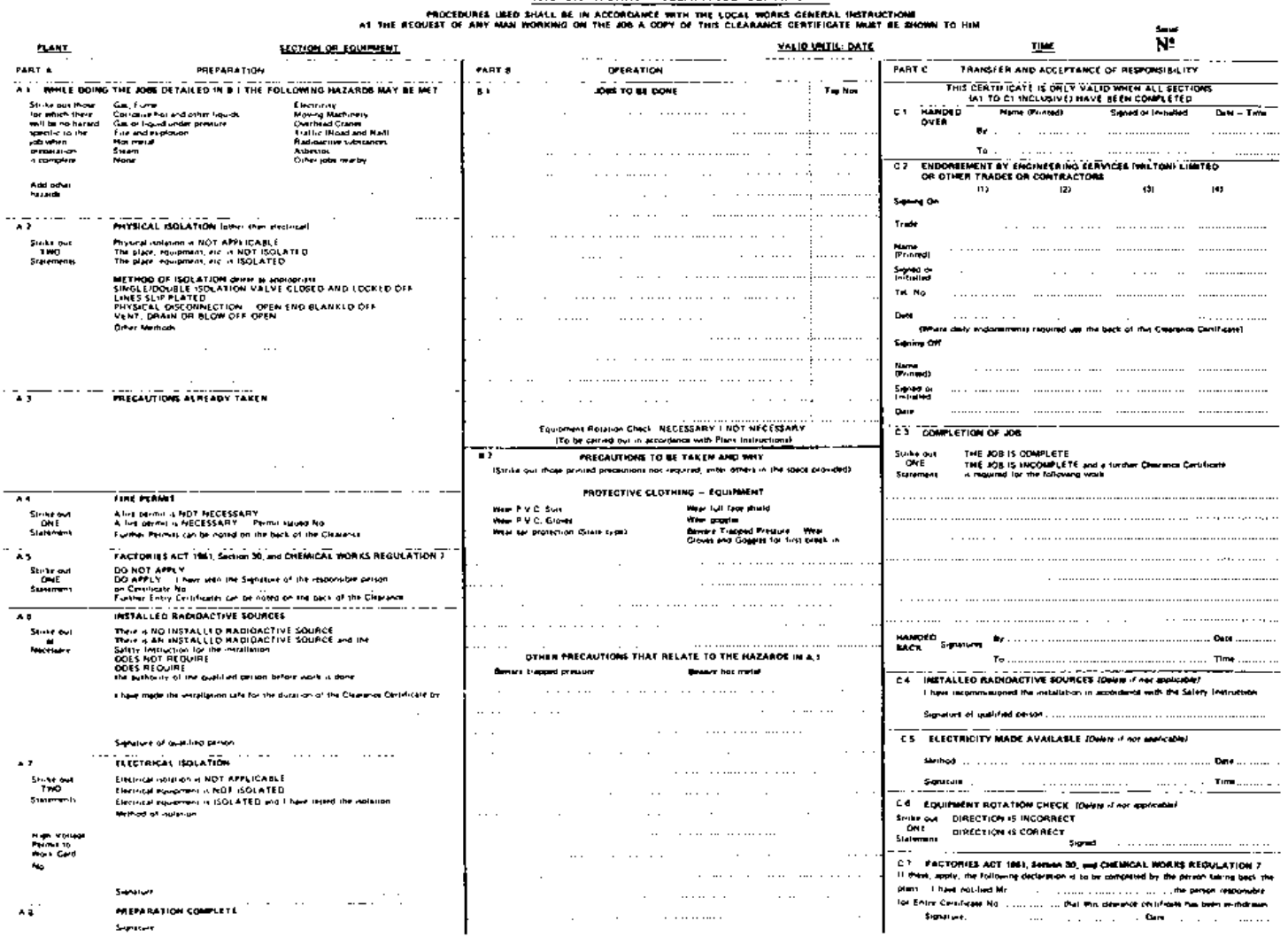
A significant proportion of accidents in vessels or confined spaces are fatal and some involve multiple deaths. The Factories Act 1961, Section 30, describes precautions which have to be taken where work has to be done inside plant in which the atmosphere is liable to be such as to involve the risk of people being overcome by dangerous fumes or lack of oxygen.

The requirements of the Act are summarized in TDN 47 for atmospheres in which dangerous fumes are liable to be present:

> No-one may enter or remain for any purpose in a confined space which has at any time contained or is likely to contain fumes liable to cause a person to be overcome unless
> (1) He is wearing a suitable breathing apparatus.
> (2) He has been authorized to enter by a responsible person.
> (3) Where practicable, he is wearing a belt with a rope securely attached.
> (4) A person keeping watch outside and capable of pulling him out is holding the free end of the rope.
>
> Alternatively, a person may enter or work in a confined space without breathing apparatus provided that
>
> (1) Effective steps have been taken to avoid ingress of dangerous fumes.
> (2) Sludge or other deposits liable to give off dangerous fumes have been removed.
> (3) The space contains no other material liable to give off such fumes.
> (4) The space has been adequately ventilated and tested for fumes.
> (5) There is a supply of air adequate for respiration.
> (6) The space has been certified by a responsible person as being safe for entry for a specified period without breathing apparatus.
>
> The person who enters the confined space must be warned when the safe period specified in (6) above will expire. In all cases a sufficient supply of approved breathing apparatus, belts and ropes, and suitable reviving apparatus and oxygen must be kept readily available, properly maintained and regularly examined.

The requirements for oxygen-deficient atmospheres are summarized in TDN 47 as follows:

> No-one may enter or remain in a confined space in which the atmosphere is liable to be deficient in oxygen unless either he is wearing a suitable breathing apparatus, or the space has been and remains adequately ventilated and a responsible person has tested and certified it as safe for entry without breathing apparatus.



WILTON WORKS – CLEARANCE CERTIFICATE

PROCEDURES USED SHALL BE IN ACCORDANCE WITH THE LOCAL WORKS GENERAL INSTRUCTIONS
AT THE REQUEST OF ANY MAN WORKING ON THE JOB A COPY OF THIS CLEARANCE CERTIFICATE MUST BE SHOWN TO HIM

PLANT | SECTION OR EQUIPMENT | VALID UNTIL: DATE | TIME | Issue No

PART A PREPARATION

A 1 WHILE DOING THE JOBS DETAILED IN B I THE FOLLOWING HAZARDS MAY BE MET

Strike out those for which there will be no hazard specific to the job when preparation is complete

Gas, Fume
Corrosive Acid and other liquids
Gas or liquid under pressure
Fire and explosion
Hot metal
Steam
None
Electricity
Moving Machinery
Overhead Cranes
Traffic (Road and Rail)
Radioactive substances
Asbestos
Other jobs nearby

Add other hazards

A 2 PHYSICAL ISOLATION (other than electrical)

Strike out TWO Statements

Physical isolation is NOT APPLICABLE
The plant, equipment, etc is NOT ISOLATED
The plant, equipment, etc is ISOLATED

METHOD OF ISOLATION delete as appropriate
SINGLE/DOUBLE ISOLATION VALVE CLOSED AND LOCKED OFF
LINES SLIP PLATED
PHYSICAL DISCONNECTION OPEN END BLANKED OFF
VENT, DRAIN OR BLOW OFF OPEN
Other Methods

A 3 PRECAUTIONS ALREADY TAKEN

A 4 FIRE PERMIT

Strike out ONE Statement

A fire permit is NOT NECESSARY
A fire permit is NECESSARY Permit issued No
Further Permits can be noted on the back of the Clearance

A 5 FACTORIES ACT 1961, Section 30, and CHEMICAL WORKS REGULATION 7

Strike out ONE Statement

DO NOT APPLY
DO APPLY I have seen the Signature of the responsible person on Certificate No
Further Entry Certificates can be noted on the back of the Clearance

A 6 INSTALLED RADIOACTIVE SOURCES

Strike out as Necessary

There is NO INSTALLED RADIOACTIVE SOURCE
There is AN INSTALLED RADIOACTIVE SOURCE and the Safety Instruction for the installation
DOES NOT REQUIRE
DOES REQUIRE
the authority of the qualified person before work is done

I have made the precautions safe for the duration of the Clearance Certificate by

Signature of qualified person

A 7 ELECTRICAL ISOLATION

Strike out TWO Statements

Electrical isolation is NOT APPLICABLE
Electrical equipment is NOT ISOLATED
Electrical equipment is ISOLATED and I have tested the isolation
Method of isolation

High Voltage Permit to Work Card No

Signature

A 8 PREPARATION COMPLETE

Signature

PART B OPERATION

B 1 JOBS TO BE DONE — Tag Nos

Equipment Rotation Check NECESSARY / NOT NECESSARY
(To be carried out in accordance with Plant Instructions)

B 2 PRECAUTIONS TO BE TAKEN AND WHY

(Strike out those printed precautions not required, write others in the space provided)

PROTECTIVE CLOTHING – EQUIPMENT

Wear P V C Suit
Wear P V C. Gloves
Wear ear protection (State type)
Wear full face shield
Wear goggles
Beware Trapped Pressure Wear Gloves and Goggles for first break in

OTHER PRECAUTIONS THAT RELATE TO THE HAZARDS IN A 3

Beware trapped pressure
Beware hot metal

PART C TRANSFER AND ACCEPTANCE OF RESPONSIBILITY

THIS CERTIFICATE IS ONLY VALID WHEN ALL SECTIONS (A1 TO C1 INCLUSIVE) HAVE BEEN COMPLETED

C 1 HANDED OVER — Name (Printed) — Signed or Initialled — Date – Time

By
To

C 2 ENDORSEMENT BY ENGINEERING SERVICES (WILTON) LIMITED OR OTHER TRADE OR CONTRACTORS

(1) (2) (3) (4)

Signing On
Trade
Name (Printed)
Signed or Initialled
Tel. No
Date

(Where daily endorsements required use the back of the Clearance Certificate)

Signing Off
Name (Printed)
Signed or Initialled
Date

C 3 COMPLETION OF JOB

Strike out ONE Statement

THE JOB IS COMPLETE
THE JOB IS INCOMPLETE and a further Clearance Certificate is required for the following work

HANDED BACK Signature By Date
To Time

C 4 INSTALLED RADIOACTIVE SOURCES (Delete if not applicable)

I have recommissioned the installation in accordance with the Safety Instruction

Signature of qualified person

C 5 ELECTRICITY MADE AVAILABLE (Delete if not applicable)

Method Date
Signature Time

C 6 EQUIPMENT ROTATION CHECK (Delete if not applicable)

Strike out ONE Statement

DIRECTION IS INCORRECT
DIRECTION IS CORRECT

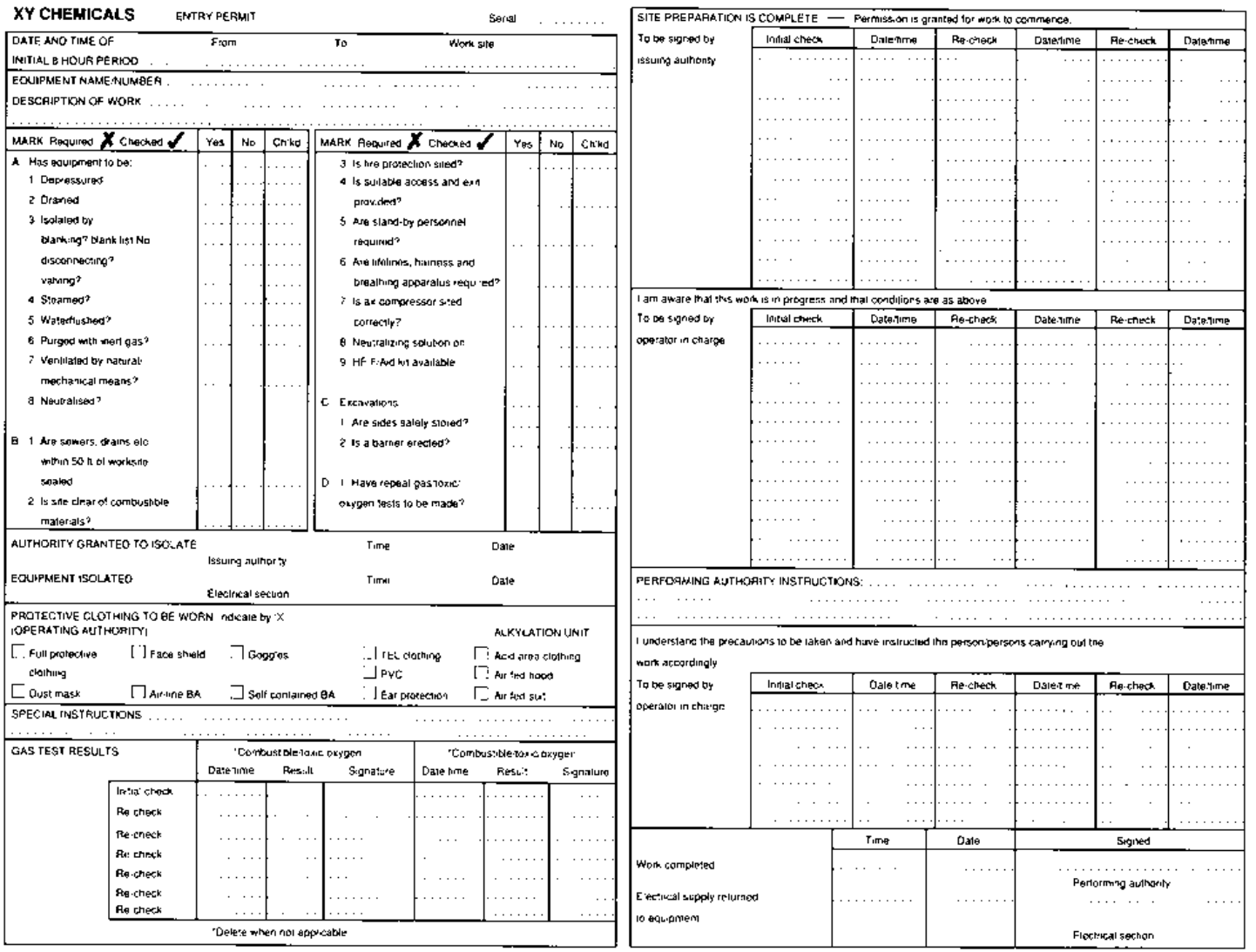
Signed

C 7 FACTORIES ACT 1961, Section 30, and CHEMICAL WORKS REGULATION 7

If these apply, the following declaration is to be completed by the person taking back the plant I have notified Mr , the person responsible for Entry Certificate No that this clearance certificate has been withdrawn

Signature Date

Figure 21.3 *Clearance certificate (Imperial Chemical Industries Ltd, 1977; reproduced by permission)*



XY CHEMICALS ENTRY PERMIT Serial . . . . . .

DATE AND TIME OF INITIAL 8 HOUR PERIOD From . . . . . To . . . . . Work site . . . . . .

EQUIPMENT NAME/NUMBER . . . . . .

DESCRIPTION OF WORK . . . . . .

MARK Required ✗ Checked ✓	Yes	No	Ch'kd
A Has equipment to be:			
1 Depressurised			
2 Drained			
3 Isolated by blanking? Blank list No			
disconnecting?			
valving?			
4 Steamed?			
5 Waterflushed?			
6 Purged with inert gas?			
7 Ventilated by natural mechanical means?			
8 Neutralised?			
B 1 Are sewers, drains etc within 50 ft of worksite sealed			
2 Is site clear of combustible materials?			

MARK Required ✗ Checked ✓	Yes	No	Ch'kd
3 Is fire protection sited?			
4 Is suitable access and exit provided?			
5 Are stand-by personnel required?			
6 Are lifelines, harness and breathing apparatus required?			
7 Is air compressor sited correctly?			
8 Neutralizing solution on			
9 HF First Aid kit available			
C Excavations			
1 Are sides safely stored?			
2 Is a barrier erected?			
D 1 Have repeat gas/toxic/ oxygen tests to be made?			

AUTHORITY GRANTED TO ISOLATE Issuing authority . . . . . Time . . . . . Date . . . . .

EQUIPMENT ISOLATED Electrical section . . . . . Time . . . . . Date . . . . .

PROTECTIVE CLOTHING TO BE WORN Indicate by X (OPERATING AUTHORITY)

☐ Full protective clothing ☐ Face shield ☐ Goggles ☐ PEL clothing ☐ PVC ☐ Ear protection ☐ Acid area clothing ☐ Air fed hood ☐ Air fed suit

☐ Dust mask ☐ Air-line BA ☐ Self contained BA

ALKYLATION UNIT

SPECIAL INSTRUCTIONS . . . . . .

GAS TEST RESULTS

	*Combustible/toxic oxygen			*Combustible/toxic/oxygen		
	Date/time	Result	Signature	Date/time	Result	Signature
Initial check						
Re-check						
Re-check						
Re-check						
Re-check						
Re-check						
Re-check						

*Delete when not applicable

SITE PREPARATION IS COMPLETE — Permission is granted for work to commence.

To be signed by issuing authority	Initial check	Date/time	Re-check	Date/time	Re-check	Date/time

I am aware that this work is in progress and that conditions are as above

To be signed by operator in charge	Initial check	Date/time	Re-check	Date/time	Re-check	Date/time

PERFORMING AUTHORITY INSTRUCTIONS: . . . . . .

I understand the precautions to be taken and have instructed this person/persons carrying out the work accordingly

To be signed by operator in charge	Initial check	Date/time	Re-check	Date/time	Re-check	Date/time

	Time	Date	Signed
Work completed			Performing authority
Electrical supply returned to equipment			Electrical section

Figure 21.4 *Entry permit (Townsend, 1992) (Courtesy of the Institution of Chemical Engineers)*

The same section of the Act also requires confined spaces to be provided with manholes and specifies minimum dimensions. Circular manholes, for example, should not be less than 18 in. in diameter or, on tank wagons and mobile plant, 16 in. in diameter. Manholes larger than these minimum sizes should be provided wherever possible. In particular, practical tests have shown the minimum size on mobile equipment to be barely negotiable by men of average build.

The control of work in vessels and confined spaces is described in TDN 47, which lists the following features:

(1) assessment;
(2) withdrawal from service;
(3) isolation;
(4) cleaning and purging;
(5) testing;
(6) certification;
(7) precautions during work –
    (a) entry without breathing apparatus;
    (b) entry where breathing apparatus is necessary;
    (c) rescue;
(8) cancellation of permit;
(9) return to service.

The issue of the permit should be done by the responsible person in accordance with the procedures described in Section 21.8.3. The issuing authority should have a sufficient familiarity with both the chemistry and the engineering aspects of the situation and should check personally the actions required.

The need for entry should be considered carefully and entry should not be made unless it is essential. The hazards of vessel entry should be reviewed, paying particular attention to any hazard arising from nearby plant and to any special circumstances or precautions.

Withdrawal from service should be a formal procedure. Operating personnel should be informed and warning notices displayed.

The isolation of the vessel should be effected in accordance with the procedures described in Section 21.4. The only method of isolation recommended for vessel entry is physical disconnection. A closed and locked valve is not an adequate method.

If there is machinery inside the vessel, such as an agitator or mixer, it should be isolated by electrical isolation or by physical disconnection. In addition, if necessary, it should be secured to prevent its moving. There may also be pumps which should be isolated electrically. The vessel should then be emptied.

Cleaning of the vessel may be effected in several ways. Steaming out is a common method. This may be preceded by washing with water, solvent or neutralizing agent. The steaming itself should be continued long enough to clean the vessel thoroughly. The steaming time is often determined by experience, but it is essential to continue steaming until the vessel is clean rather than simply for a pre-determined time. It is important to ensure that equipments attached to the main vessel are also cleaned thoroughly. The period of steaming and the completion of steaming should be checked by the responsible person. If several hours elapse after steaming, it is advisable to steam the vessel again immediately before entry. It should be ensured that the steaming itself is done safely and without either overpressuring the vessel with steam or causing it to collapse under the vacuum created by steam condensation.

Other cleaning methods include thorough washing with cold or hot water or with solvents or neutralizing agents and boiling with water. Some cleaning agents such as solvents can create a secondary hazard and may themselves need to be removed by steaming. Boiling water cleaning requires precautions against overpressure and vacuum collapse of the vessel.

It is sometimes necessary to resort to hand cleaning to remove sludge and residues. In such cases it is essential to work with the full precautions of breathing apparatus, a safety line, and rescue equipment and personnel.

On the completion of cleaning all liquid should be run out and the manholes opened for ventilation. If steam cleaning has been used, opening of the manholes while the vessel is hot assists air circulation by natural convection. It may be necessary, however, to use forced ventilation from a blower or compressed air line.

If the vessel is hot, it should be allowed to cool before any entry is made.

If the vessel has contained a flammable gas or vapour, it may be purged with an inert gas such as nitrogen or carbon dioxide. This then creates, however, an asphyxiation hazard. It is thus necessary to purge the inert gas with air.

Testing of the atmosphere in the vessel should be carried out before it is certified as safe to enter or before the safety precautions for entry are specified. The tests should check the presence of toxic and/or flammable fumes and, if necessary, the adequacy of the oxygen content. The tests should be conducted by a competent person. If the work is at all prolonged, the tests should be repeated.

The general testing of working atmospheres is dealt with in Chapter 25 and is therefore not considered here. As far as testing in vessels is concerned, entry into the vessel should be avoided if possible. Instead samples should be drawn from inside the vessel through sample tubes. It is essential, however, to test throughout the vapour space; factors which may cause this not to be homogeneous include release of fumes from sludge or residues and layering of inert gases.

If entry into a vessel for testing is unavoidable, this should be done with the foil precautions of breathing apparatus, a safety line, and rescue equipment and personnel.

With regard to the permissible concentration of toxic materials it has been common practice for many years to use the threshold limit value (TLV). The current equivalent would be the relevant exposure limit. TDN 47 states, however, that the TLV is not necessarily applicable in confined spaces and suggests that in view of the possible variations in concentration and/or increases while the work is in progress a somewhat more conservative value may be advisable.

When the above stages have been completed, the responsible person can take a decision on the precautions to be taken on entry and, in particular, whether (1) entry is safe for a specified period without breathing apparatus or (2) entry requires breathing apparatus, a safety line and other precautions.

Certification can then be effected by the issue of a permit-to-work detailing the safety measures already taken (e.g. isolation, cleaning and purging, testing), those to be taken (e.g. ventilation, repeat testing, breathing apparatus, a safety line, and rescue equipment and personnel) and the period of validity.

Precautions during the work depend on whether the method of entry involves the use of breathing apparatus or not. If breathing apparatus is not used, good ventilation is essential. This means at least several changes of air per minute. If there are sufficient top and bottom openings, natural ventilation may suffice, but more usually forced ventilation is necessary using compressed air or blowers. The air line or blower trunking should extend to the bottom of the vessel to assure the removal of heavy fumes and give good air circulation. If there is a static electricity hazard, it may be necessary to bond the air line or trunking to the metal of the vessel. Gaseous oxygen should not be introduced into the vessel to increase the oxygen content of the atmosphere, since it creates the hazard of an oxygen-enriched atmosphere.

If breathing apparatus has to be used, it should be either the self-contained breathing apparatus type or the air line type. Canister respirators should not be used, because they give inadequate protection against high concentrations of toxic flumes and are useless in atmospheres deficient in oxygen.

The person entering the vessel should also wear a safety harness and lifeline wherever practical. The free end of the line should be held by a person outside. The harness should be worn so that the worker can be pulled head first up through the opening.

It is the duty of the person outside, or safety watch, to keep hold of the safety line and observe the person working inside the vessel. He should have a means of summoning assistance rapidly. If possible, there should also be other workers nearby.

If the person in the vessel is overcome, the safety watch should raise him head first through the opening. An unconscious man is a heavy weight and the safety watch should have both adequate strength and training for his task.

There should be rescue equipment, such as additional breathing apparatus and safety lines and reviving equipment and medical oxygen.

The restrictions on entry apply also to entry for rescue. In addition, if entry has been permitted without breathing apparatus and the person inside has been overcome, entry for rescue should be made only wearing breathing apparatus and a safety line and with other personnel available to give assistance. Multiple fatalities have occurred where men have gone in to rescue their fellows without proper protection.

When the work is finished, the equipment used should be removed, the work site should be inspected and the permit cancelled in accordance with the procedures given in Section 21.8.3.

Personnel should be warned that the vessel is no longer safe for entry. Accidents occur due to persons entering vessels which are no longer safe in order to recover tools, etc.

The de-isolation of the vessel should be effected in accordance with the procedures described earlier and the vessel returned to service.

21.8.9 Types of permit system

The normal permit system is a single-stage system in which there is a single permit issued by the issuing authority to the performing authority. As stated earlier, the norm is that the issuing authority is the operations supervisor and the performing authority the person who is to do the work, but in some cases the performing authority is the maintenance supervisor.

There are, however, variations on this system. In some companies, certain permits are issued by the safety officer.

In a particular permit system a given job may require more than one document. There may well be other certificates which are necessary before the main permit can be issued. One example is an isolation permit, in a system where separate permits are used for isolation, and deisolation. Another is a test certificate for analysis of the working atmosphere.

Some types of permit relate to higher levels of hazard than others, so that there can be a hierarchy of permits.

21.8.10 Design of permit systems

The effectiveness of a permit system depends in large part on the way in which the system is designed and operated.

Aspects of the design of a permit system include (1) standardization, (2) the personnel involved, (3) scope, (4) cross-referencing, (5) display, (6) multiple jobs, (7) change of intent, (8) suspension, (9) handback, (10) training and (11) monitoring, auditing and review.

It is desirable that the permit system used within a company be as uniform as is practicable. This applies not just to the design of permit forms but to the whole system. A standard system eases the problem of training and reduces the probability of confusion and hence error.

There are constraints, however, on complete standardization. A permit system is a means of communication between the interested parties and must therefore reflect the organizational structure. It is also a formalization of the operating and maintenance procedures. Whilst uniformity is desirable, a mismatch between the permit system and either this structure or the procedures is too high a price to pay, in that it is likely to undermine acceptance of the permit system and hence compliance with it. Standardization of the permit system in the North Sea was urged on the Piper Inquiry, but the latter did not recommend this.

The personnel involved in the issue of a permit should be identified. In some systems the number may be quite large, perhaps as high as 15–20.

There may be a requirement that in certain defined cases where work at a particular plant may affect an adjacent plant, the operations supervisor on that plant should countersign the permit.

The permit should ensure that the scope of the work to be done is fully defined.

The design of the permit form should allow for the necessary cross-referencing. There should be cross-references to: other jobs, by description of job as well as permit number; isolations and the associated permit numbers; and equipment identification tags. In particular, the cross-referencing should cover the case where isolation is common to more than one job.

A copy of the permit should be clearly displayed in the main control room or permit co-ordination room, with

additional copies at local control rooms. Another copy should be displayed at the work site, except when the job is done at a number of locations, in which case it should be kept by the person in immediate charge of the work. If this person is not also the performing authority, the latter should also have a copy.

For a given equipment, there should be only one permit in force, but it may cover work by more than one trade.

It not infrequently happens that there is a change of intent while the job is being done. An example is a change from work on pump beatings which does not involve breaking into the process line, to other work which does. If such a change of intention occurs, a separate permit should be issued.

It may well happen that it is necessary to suspend the work. This can occur because: work is carried out only for one shift each day; spares have to be awaited; the activity is incompatible with another which has higher priority, as with suspension of hot work whilst a flammable gas sample is taken; or there is an emergency.

One option is that the permit is then cancelled so that resumption of the work requires a fresh permit. This may well be the best policy if the work is being suspended for an undefined and possibly extended period and the plant can be rendered safe. Alternatively, the permit itself may be suspended. If this option is taken, the permit should be clearly displayed in a suitable place and clearly marked as suspended; the condition in which the plant has been left and the consequences for other activities should be stated; and prior to reactivation the issuing authority should verify that it is safe for the work to proceed. The OIAC *Permit System Guide* gives further guidance on the procedures for the suspension of a permit.

A suspended permit was at the centre of the events which led to the Piper Alpha disaster and the view was then urged that the suspension of a permit should not be an option. The Inquiry recognized the dangers but did not recommend prohibition.

The procedures for handback of the permit, described earlier, should be clear.

The permit system should ensure that both operations and maintenance personnel, company employees as well as contractors are trained in the system which applies at the actual plant where they work. It is not enough to have instruction in the general principles of a permit system; personnel must be clear about the details of the operation, and the reasons for, the particular permit system governing their own work.

There should be built into the permit system arrangements to ensure that the operation of the system is monitored regularly and is subject to a more searching audit at specified intervals, and that a review of the appropriateness of the system is undertaken at specified, longer intervals.

21.8.11 Operation of permit systems

If the permit has been well designed, the operation of the system is largely a matter of compliance. If this is not the case, the operations function is obliged to develop solutions to problems as they arise.

As just stated, personnel should be fully trained so that they have an understanding of the reasons for, as well as the application of, the system.

It is the responsibility of management to ensure that the conditions exist for the permit system to be operated properly. An excessive workload on the plant, with numerous modifications or extensions being made simultaneously, can overload the system. The issuing authority must have the time necessary to discharge his responsibilities for each permit.

In particular, he has a responsibility to ensure that it is safe for maintenance to begin and to visit the work site on completion to ensure that it is safe to restart operation.

Where the workload is heavy, the policy is sometimes adopted of assigning an additional supervisor to deal with some of the permits. However, a permit system is in large part a communication system, and this practice introduces into the system an additional interface.

The communications in the permit system should be verbal as well as written. The issuing authority should discuss, and should be given the opportunity to discuss, the work. It is bad practice to leave a permit to be picked up by the performing authority without discussion.

The issuing authority has the responsibility of enforcing compliance with the permit system. He needs to be watchful for violations such as extensions of work beyond the original scope.

21.8.12 Deficiencies of permit systems

An account of deficiencies in permit systems found in industry is given by S. Scott (1992). As already stated, some 30% of accidents in the chemical industry involve maintenance and of these some 20% relate to permit systems.

The author gives statistics of the deficiencies found. Broadly, some 30–40% of the systems investigated were considered to be deficient in respect of system design, form design, appropriate application, appropriate authorization, staff training, work identification, hazard identification, isolation procedures, protective equipment, time limitations, shift change procedure and handback procedure, whilst as many as 60% were deficient in system monitoring.

21.8.13 Audit of permit systems

It is not enough to create a permit system to control maintenance work. There should also be arrangements for the audit of the system to ensure that it is operating properly. These may consist of a specific instruction to the plant manager to check each week a proportion of the permits issued.

21.8.14 Checklist for permit systems

The OIAC *Permit Systems Guide* gives a checklist for permit systems. This is shown in Table 21.3.

21.9 Maintenance Equipment

21.9.1 Tools

Tools such as hammers and spanners have been considered a possible source of ignition, and so-called non-sparking tools have been developed. Materials used

Table 21.3 *A checklist for permit-to-work systems (Oil Industry Advisory Committee, 1991) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

The purpose of this checklist is to help everyone concerned with the preparation of permit-to-work systems to decide whether a particular example covers all the points which are considered essential. If the answer to any of the questions below is 'no', the system may need to be reconsidered and changed.

The system

1 Does the permit system in force satisfy all the legal requirements applying to that site or installation?
2 Is the permit system recognized throughout the site or installation as being essential for certain types of work?
3 Are the types of work, types of job or areas where permits must be used clearly defined and known to all concerned?
4 Does the permit system extend to contractors and their employees?
5 Is it clearly laid down who may issue permits?
6 Is it clearly laid down how permits should be obtained for specific jobs?
7 Is the permit system flexible enough to allow it to be applied to other potentially hazardous work, apart from that which may have been specifically identified when the system was established?
8 Is the issue of a permit by a person to themselves prevented?
9 Does the system provide both for the recipient to retain the permit and for a record of live permits and suspended permits to be maintained at the point of issue?
10 Does the system require a copy of the permit to be displayed at the workplace?
11 Does the system require the display of live and suspended permits so that process operating staff can readily see and check plant status?
12 Is there a set of properly documented isolation procedures for working on potentially dangerous items of plant and does it provide for long term isolation?

Training and competence

13 Is the permit system clearly covered during site or installation safety induction training?
14 Are personnel who have special responsibilities under the permit system, e.g. issuing and isolating authorities, properly authorized and trained to undertake the duties required of them?
15 Do these people have sufficient time to carry out these duties properly?
16 Does the system require formal assessment of competence of personnel before they are given responsibilities under the permit procedure?
17 Is a record of training and assessment maintained?
18 Do training and competence requirements include contractors?
19 Are individuals provided with written confirmation of successful completion of relevant training and are these documents checked before appointments are made within the permit-to-work system?

The permit

20 Is there a clear requirement for work being done under a permit to be stopped if any new hazards have arisen or old hazards recurred?
21 Does the permit contain clear rules about how the job should be controlled or abandoned in the event of an emergency?
22 Do permits specify clearly the job to be done?
23 Do permits specify clearly to whom they are issued?
24 Does the system require the potential hazards at the work site to be clearly identified and recorded on the permit?
25 Does the permit clearly specify the precautions to be taken by the issuing and performing authorities?
26 Do permits specify clearly the plant or geographical area to which work must he limited?
27 Does the recipient have to sign the permit to show that they both read the permit and understood the conditions laid down in it?
28 Do permits specify clearly a time limit for expiry or renewal?
29 Does the permit include a handover mechanism for work which extends beyond a shift or other work period including work which has been suspended?
30 Is a handback signature required when the job is complete?
31 Is there a procedure to bring to the attention of the site manager tasks which require inhibiting safety devices, e.g. fire detectors, to ensure that contingency plans and precautions are in place?

Co-ordination

32 Are copies of permits issued for the same equipment/area kept and displayed together?
33 Is there a means of co-ordinating all work activities to ensure potential interactions are identified?
34 Is there provision on the permit form to cross-reference other relevant certificates and permits?
35 Is there a procedure to ensure that the agreement of others who could be affected by the proposed work is obtained before starting the work or preparations for it?
36 Where there are isolations common to more than one permit, is there a procedure to prevent the isolation being removed before all the permits have been signed off?

Monitoring

37 Is there a system of spot checks to ensure that permits are being followed?
38 Is there a procedure for reporting any incidents that have arisen during work carried out under a permit and for reviewing procedures as necessary?
39 Are audits carried out on the permit-to-work system at least once a year, preferably by people not normally employed at that site or offshore installation?

in such tools are, typically: aluminium, bronze or monel, for tools that have to withstand impact or torque such as hammers, spanners and crowbars; copper–beryllium alloy, for tools requiring a cutting edge or gripping teeth such as knives, chisels, saws, drills, pliers and shears; and plastics, leather, fibre and wood, for shovel and scraper tools.

These tools have a number of disadvantages. Generally, they are more expensive and they are softer and tend to burr. Moreover, particles can more easily become embedded in them, thus reducing their non-sparking qualities.

The American Petroleum Institute (API) has issued a number of reports over a period of years on the appropriateness of using non-sparking tools in petroleum operations. The general conclusion is that an incendive spark of steel would be unlikely to be produced manually and that power operation would be needed. Its current position is stated in API Publ. 2214: 1989:

> The Institute's position is that the use of special nonferrous handtools, sometimes referred to as nonsparking tools, is not warranted as a fire-prevention measure applicable to petroleum operations.

Certain gases handled in the chemical industry are particularly susceptible to spark ignition, notably hydrogen, acetylene, ethylene and carbon disulphide. One policy described on non-sparking tools in this industry is that instead of utilizing all types of non-sparking tool in flammable areas a more limited use is made, restricting their application to the use of non-sparking hammers (though not spanners) for the hardening up of joints on lines containing the above four gases.

The extent to which tools may act as ignition sources is discussed in more detail in Chapter 16.

21.9.2 Lifting equipment

Lifting equipment has been the cause of numerous accidents. There have long been statutory requirements, therefore, for the registration and regular inspection of equipment such as chains, slings and ropes. These are given in the Factories Act 1961, Sections 22–27, and in the associated legislation, including the Chains, Ropes and Lifting Tackle (Register) Order 1938, the Construction (Lifting Operations) Regulations 1961 and the Lifting Machines (Particulars of Examination) Order 1963. Some of these regulations are superseded by the consolidating Provision and Use of Work Equipment Regulations 1992. Only properly registered and inspected equipment should be used for lifting.

In process plant work incidents sometimes occur in which a lifting lug gives way. This may be due to causes such as incorrect design or previous overstressing.

21.9.3 Mobile cranes

Mobile cranes present several different types of hazard. One is that of collision with process plant, particularly pipebridges, when the crane is on the move. A minimum measure to prevent this is clear identification of pipebridges, but it may be advisable to resort to more positive protection, such as a crossbeam in front of the pipebridge which obliges the driver to lower the jib.

Another type of hazard is the overturning of the crane onto process plant. For a given crane there is a maximum sale load and maximum safe jib radius. There is normally a safe load indicator, but nothing to indicate the safe jib radius. If the latter is exceeded, the jib itself constitutes the main load and a small additional load may be enough to topple the crane. An incident involving the overturning of a crane is described in Case History B57.

It is important for crane drivers to be well trained in the operation and limitations of their cranes and in the special hazards of process plants.

A rather less obvious hazard in cranes hired from outside contractors is the use of cab heaters which are not suitable for hazardous areas. A heater is needed, but it should be of an appropriate type.

21.9.4 Lift trucks

Lift trucks, including forklift trucks, present another set of hazards. One is the hazard due to any moving vehicle, especially in a relatively congested plant area.

A specific aspect of this is impact on plant. Incidents are numerous in which lift trucks are driven into and damage buildings and plant, including process plant; pipework is particularly at risk. Impact is more likely if the truck is travelling with arms extended. A lift truck may also run over and crush pipework or cabling.

Overturning is another hazard, the causes of which include misloading, sudden braking or sharp turning and traversing of rough or sloping terrain.

A lift truck is a vehicle with projecting and moving parts. It therefore has some of the characteristics of a machine. The power source, batteries or engine, on a lift truck may act as a source of ignition.

Guidance on lift trucks is given in HS(G) 6 *Safety in Working with Lift Trucks* (HSE, 1992). HS(G) 6 states that lift trucks are responsible for about one-third of the 20 000 reportable injuries each year which involve transport. In the period 1986–1991, 112 people were killed in accidents involving lift trucks.

Prevention of lift truck accidents requires in particular attention to (1) plant layout, (2) working practices and (3) training. Specific preventive measures fall mainly under the following headings: (1) traffic, (2) imbalance, (3) impact and crushing and (4) moving parts.

Measures which address the traffic aspects include the layout of the lift truck workplace, use of driving practices which specifically address lift truck dangers, limitation of driving to trained personnel, avoidance of obscuration of the driver's view by the load and removal of people from the vicinity of the truck, using both segregation and warning devices. Prevention of imbalance requires the application of loading rules and avoidance of unsuitable terrain. Measures to prevent impact include use of layout and barriers and travelling with lift arms lowered. The danger from working parts may also be minimized by suitable layout and working practices.

21.9.5 Robots

A less conventional form of equipment is a robot. The use of robots in relation to process equipment is most developed in the nuclear industry and in offshore activities, but a gradual growth of their use in special applications on conventional process plants can be envisaged.

Accounts of robots are given by Collins (1982), T.J. Williams (1983), Siddle (1986b) and R.M. Taylor and Lewis (1987). HSE guidance on robots is given in HS(G)

43 *Industrial Robot Safety* (1988) (the HSE *Robot Safety Guide)*.

The term 'robot' has been used to describe a variety of devices. The definition given by the Robot Institute of America (RIA) is a 'reprogrammable, multifunctional manipulator designed to move materials, parts, tools or specialized devices through variable preprogrammed motion for the performance of a variety of tasks'. The Japanese Industrial Robot Association defines four levels of complexity in robots. The first level is a manual manipulator which performs preset sequences; a typical application is as a means of remote manipulation in hazardous environments. The other three levels are playback robots, numerically controlled robots and intelligent robots. A robot is distinguished from a manual manipulator by its program, and from the single-task devices used in much factory line production by its flexibility.

Features of a robot are the program, the control system, the power, the sensors, the axes of movement and the lifting capacity. A common form of control system is one in which the robot is taken through a sequence under manual guidance, the sequence is repeated automatically to check it out and it is then committed to memory.

Industrial applications include robots which perform the operations of pick-and-place, spraying and painting, resistance welding, continuous path welding, and assembly. The more advanced applications of robots depend heavily on the availability of suitable sensors, both contact and non-contact types.

The use of robots to reduce exposure of personnel at a nuclear plant is described by R.M. Taylor and Lewis (1987). They use the term 'robot' to include non-programmable remotely operated manipulators and a large proportion of the robots used are evidently of this type. Three applications are described. One is a bagout facility robot and another is a sampling aisle robotic system. In both cases the point-to-point movement is programmed whilst the operator selects and monitors the sequence of moves. The third application is a large robotic system used to dismantle obsolete equipment. This consists of a five-axis manipulator integrated with a three-axis gantry serving a $70 \times 20 \times 20$ ft work area. The operator can operate the manipulator by remote control as well as carry out sequences under automatic control.

Robots may be used to relieve humans of tasks which involve a degree of hazard, and this is likely to be a principal use in the process industries. They do, however, bring their own hazards in that a robot is both powered and capable of movement.

HS(G) 43 deals primarily with the fixed 'teach and play back' type of robot. For the purposes of the treatment given, the guide takes the term to mean 'a manipulating device which is automatically controlled, is reprogrammable and is capable of serving a number of different purposes'. It deals with robot safety under the following headings: (1) safeguarding robot systems, (2) safety in design and manufacture, (3) safety during installation and commissioning, (4) safety during use, (5) safety during programming and (6) safety during maintenance. It also deals with training for robot safety and gives a number of appendices which cover *inter alia* hazard identification and risk assessment, safeguarding methods, and case studies.

The hazards posed by a fixed robot are those of a machine, essentially striking and trapping and entanglement. The characteristic problem with a robot is the realization of these hazards due to aberrant behaviour. Two potential causes of such behaviour are power transients and program errors.

The approach to the safeguarding of robot systems described in HS(G) 43 is based on: hazard identification, including failure modes and effects analysis; formulation of strategies of hazard elimination and mitigation; definition of levels of integrity for the safety controls and interlocks; and risk assessment for the system as a whole.

The conventional methods of machine guarding, described in BS 5304 and also BS 2771 and BS 6491 and PM 41, are in large part applicable to robots also. Their application is considered in Appendix 2 of the Guide.

These may be complemented by critical examination of the need for close approach to the robot and the development of a suitable strategy for situations where close approach is unavoidable, the principal elements of which are that the robot should be operated at low speed and that its control should rest in the hands of the person who is to approach it.

There are a number of features which can be incorporated in the design of a robot to minimize hazards. Trapping points should be avoided. Variable speed controls and a facility for single stepping should be provided and the control pendant ergonomically designed. The robot should have brakes and/or hydraulic stop valves to arrest movement. The arcs of movement of the robot's arms should be restricted, and suitable stops, fixed or adjustable, provided. Another precaution is limitation on the forces which can be exerted by the arms. A gripper should be designed so that it can cope with the static and dynamic forces created by the load, including emergency stop, and so that it does not release the load on power failure. The design should provide a parking position and should cater for the return of the robot to normal operation after different types of interruption, with movement always being by a specified trajectory. The Guide also details numerous aspects of the design of the control pendant. The robot should be supplied with high quality documentation. Design aspects of the overall robot system include a layout to facilitate viewing and the use of interlocks.

The robot system should be subject to suitable methods of hazard identification and risk assessment, as described in Appendix 1 of the *Guide*. The hazard identification should include a review of the states of the robot, its functions and its interaction with the plant.

With respect to installation and commissioning aspects of robot safety, HS(G) 43 deals mainly with the development of safe working procedures. The safe use of a robot largely centres around control of access. A fixed robot generally operates in a 'cell', the access to which is controlled using appropriate methods of safeguarding Appendix 2 of the Guide describes the various options. The approach taken follows that of BS 5304, which details the methods and gives an approach to selection based on the level of risk. Basic protection is

provided by perimeter fencing and interlocks. Electrosensitive safety systems are available utilizing various forms of proximity sensor such as photoelectric (PE) devices, capacitance devices and pressure sensitive mats. Other safety devices include: trips and emergency stops; brakes; positive stops; and enabling controls, or devices working on the dead man's handle principle. A form of the latter suited to robots is the two-hand control, requiring the use of both hands, which it thus protects.

Safety is also a consideration in the programming of the robot. For this HS(G) 43 refers to the guidance given in the HSE *PES Guide*.

Safe maintenance of a robot requires well thought out maintenance procedures and precautions to prevent sudden, unpredictable movements.

Robot case studies given in HS(G) 43 include a robot serving in a machine installation, robot arc welding and robot water jetting.

21.10 Flanged Joints

21.10.1 Making joints

The normal pipe joint on a process plant is the flanged joint, as described in Chapter 12. The two main varieties are the gasketed joint and the ring-type joint. For high pressures it is the latter which is used.

Accounts of the making up of flanged joints, and in particular of bolt tightening, are given by Graves (1966), Briscoe (1976), K. Gibson (1986) and Garner (1993).

The joint to be made up may be between two sections of pipe, between a section of pipe and some other item of plant such as a valve or pump or between a section of pipe and a blind flange, closing off the end of the pipe.

If the joint is a gasketed one, the surfaces of the flanges should be free of deterioration and clean, and the gasket used should be of the correct type. Metallic spiral wound gaskets in particular should not be reused.

In the case of a ring-type joint, the surfaces of the flanges should again be free of deterioration and clean, and the ring used should be of the correct type and new.

The bolts or studs used should be those specified in all relevant respects. They should be of the correct diameter and length and material of construction. The nuts likewise should be of the right material.

The pipe or other equipment to which the flanges to be joined are attached should be properly supported and aligned so as to facilitate the making of the joint.

In making up a flange, it is bad practice to tighten all the bolts on one side, then the belts on the other side. The proper procedure is sequence tightening, which involves gradual tightening of the bolts following a criss-cross pattern.

There are a number of methods of tightening the bolts. Taking the case of a ring-type joint, one is to screw the nuts on until they are finger tight. This method is suitable for attaching a blind flange for the purpose of keeping out dirt, but not as a method of making up a leak-tight flange. A flange may be made up hand tight by tightening with a spanner or it may be flogged up using a flogging spanner and hammer. The latter method gives a more leak-tight joint and in some applications is the required method.

The bolt tightnesses obtained by such methods are variable and there is a trend to the use of more sophisticated methods, as described by K. Gibson (1986). Three basic methods are available, two involving cold tightening and one hot tightening. The first cold tightening method is the regular one of rotating the nut against the thread helix angle. The other is to stretch the bolt longitudinally, index the nut and release the stretching load. The hot tightening method is to heat the bolt, causing it to undergo thermal expansion, index the nut and let the bolt cool down.

There are a variety of tightening tools available. They include: traditional spanners and torque wrenches, where the applied torque varies with the length of the lever arm; impact wrenches, either hydraulic or pneumatic; pneumatic torque multipliers; and hydraulic torque wrenches. There are various bolt stretching devices, notably direct-acting bolt tensioners. Likewise, there are a variety of techniques for measuring bolt stress. One of the simplest is the micrometer, which measures strain, from which stress may then be calculated.

In order to stretch a bolt accurately by a torque method it is necessary to exercise accurate control of the torque and to know the coefficient of friction of the thread and nut-set interfaces. Alternatively, the tension may be determined by measurement as just described.

As indicated, a bolt or stud has a design pre-tension or pre-stress. This pre-stress should be such that the bolt is not stretched beyond the elastic limit. In this condition the bolt acts like a spring. It then exerts on the flange the rated damping force. If the pre-stress is too low, the bolt may work loose. If it is too high, the bolt may yield or fracture.

The pre-stress is obtained by the application of torque. However, as indicated, a large proportion of the torque is lost in friction of the thread, under the bolt head and/or the seating surface of the nut. Garner (1993) estimates this proportion as 60–90%. The bolt manufacturer provides data on the relation between torque and pre-stress, but these are necessarily based on average values for the friction.

As described by this author, lubrication may be used to reduce the friction and to give more uniform tensioning. The lubricant should be matched to the application, selection being a specialist matter.

A particular problem in bolt tightening is that of leaks on heat exchangers, which is discussed by Briscoe (1976). He quotes the results of experiments using both hand wrenches and flogging hammers, showing the unreliability of standard torque–tension relations. On one of his graphs the lowest stress is 43 000 psi and the highest 120 000 psi. He indicates that in heat exchanger work for studs larger than 1 in. in diameter the only method found to be reliable is hydraulic stud tensioning.

This author draws attention to a number of problems with studs on heat exchanger flanges. One is differential expansion of the flange itself and of the stud, equivalent in the example quoted to a differential force of 21 000 psi. Another is the difference in the temperatures of studs at different positions on the flange, with the air beneath the flange cold but that above it hot; in one case quoted the temperatures of the studs at the 6 and 12 o'clock positions were 220°F and 440°F, respectively, which is equivalent to a differential force of more than 45 000 psi. Another feature is the effect of insulation on stud temperature.

On 26 May 1983 at Bloomfield, New Mexico, a compressor head gasket ruptured, resulting in a gas leak and an explosion in the compressor house (Case History A105). The investigation report (NTSB, 1983 PAR-83–04) found that the bolts on the compressor head flange had been improperly tightened and that there were wide variations in the bolt tightnesses.

The leak-tightness of a blind flange on the end of a pipe was a key issue at the Piper Alpha Inquiry (Cullen, 1990). Evidence given included: an account of the making up of a joint, and in particular the different methods of bolt tightening (Ritchie, 1989; Whalley, 1989); experimental measurements of bolt stretch vs torque, which illustrated the variability of the bolt extensions (Davie, 1989); and measurement of the torques obtained by hand tightening and by flogging up (Standen, 1989).

One of the potential leak scenarios considered at this inquiry was a leak due to failure of bolts on the reciprocating compressors (Bett, 1989). Inspections in the first half of 1988 revealed that on one cylinder on the A machine 7 stud bolts out of 16 had failed. The condition was described by the expert witness as potentially serious. An inspection of a cylinder on the B machine 4 months later found 5 failed bolts.

Defects in flanged joints include: the use of incorrect or detective bolts, studs or nuts; the use of incorrect or defective gaskets or rings; undertightening of the bolts so that the joint is not leak-tight; overtightening of the bolts so that they are overstretched; and subjecting the bolts to additional stresses.

It is not unusual for a flanged joint to leak. A common response is to tighten the bolts. This may be effective if the bolts were loose in the first place. However, further tightening of bolts which were correctly tensioned originally is bad practice. The National Transportation Safety Board (NTSB) report states:

> Bolted assemblies should not be tightened under pressure. *Never* 'tighten down' a leaking gasket in an assembly that is properly torqued. The assembly should be taken apart and inspected for causes of the leak and a new gasket installed on reassembly.

Another incorrect response to a leaking flange is the use of larger, strong bolts. As explained by Graves (1966), this is liable to make the flange bow and to exacerbate the leak.

21.10.2 Breaking joints

Breaking into a pipeline in a chemical works can involve a number of hazards and it is necessary to exercise considerable care. Safe methods for the breaking of pipelines are described in *Safety in Inspection and Maintenance of Chemical Plant* (BCISC, 1959/3).

For the breaking of a pipeline there should be clear instructions on the work and on the area in which it is to be done. Information should be given on the material in the line and its hazards, and on the precautions to be taken. The joint to be broken should be indicated by an identification tag. The work is normally covered by a permit-to-work.

Some preliminary measures and precautions include:

(1) isolation of the working area and posting of warning notices;
(2) provision of safe access;

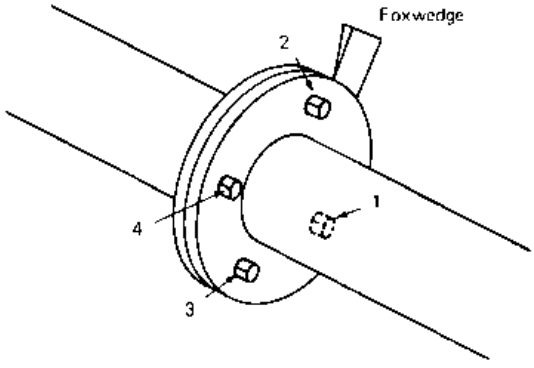


Figure 21.5 *Sequence of operations in breaking a flanged joint*

(3) support of the pipe on either side of the joint;
(4) isolation of the pipe section;
(5) release of pressure from the pipe section;
(6) draining of the pipe section and disposal of the fluid drained;
(7) precautions against fire;
(8) protection of personnel.

The joint to be broken should be isolated. Pumps and other devices which could put the joint under pressure should be switched off. Measures should be taken to release the pressure in the line.

It should be assumed, however, that the pipe may be full and under pressure, and precautions should be taken accordingly. In particular, it may be necessary to use protective hoods or equivalent equipment.

There is a correct way to break a joint. The principle is to loosen adjacent nuts and bolts first so that they can be retightened quickly if necessary. The loosening should be done slowly and continuously. The preferred sequence is shown in Figure 21.5. Bolt 1, which is the furthest away, is slackened first, then bolts 2 and 3. Bolt 4, which is the nearest, should not be slackened until the foxwedge has been used to open the joint and drain the line completely.

Some joints are difficult to break and thus constitute a potential hazard. A persistently troublesome joint should be reported by the maintenance personnel. An alert supervisor will recognize such a joint as a problem.

The pipework designer also has a contribution to make by building into the design enough 'spring' to facilitate the breaking of joints which must be broken frequently. Alternatively, a slip ring may be installed.

It can occur that a bolt, or stud, breaks whilst it is being undone. The correct procedure for dealing with a broken bolt, in a single isolation situation, is to replace it with a new one before proceeding.

The danger of not following this procedure is illustrated by the following incident (Anon., 1977 LPB 14, p. 2), which occurred during the breaking of a flange on a liquefied petroleum gas (LPG) main at 200 psig. As the joint was being broken, a first stud snapped, the

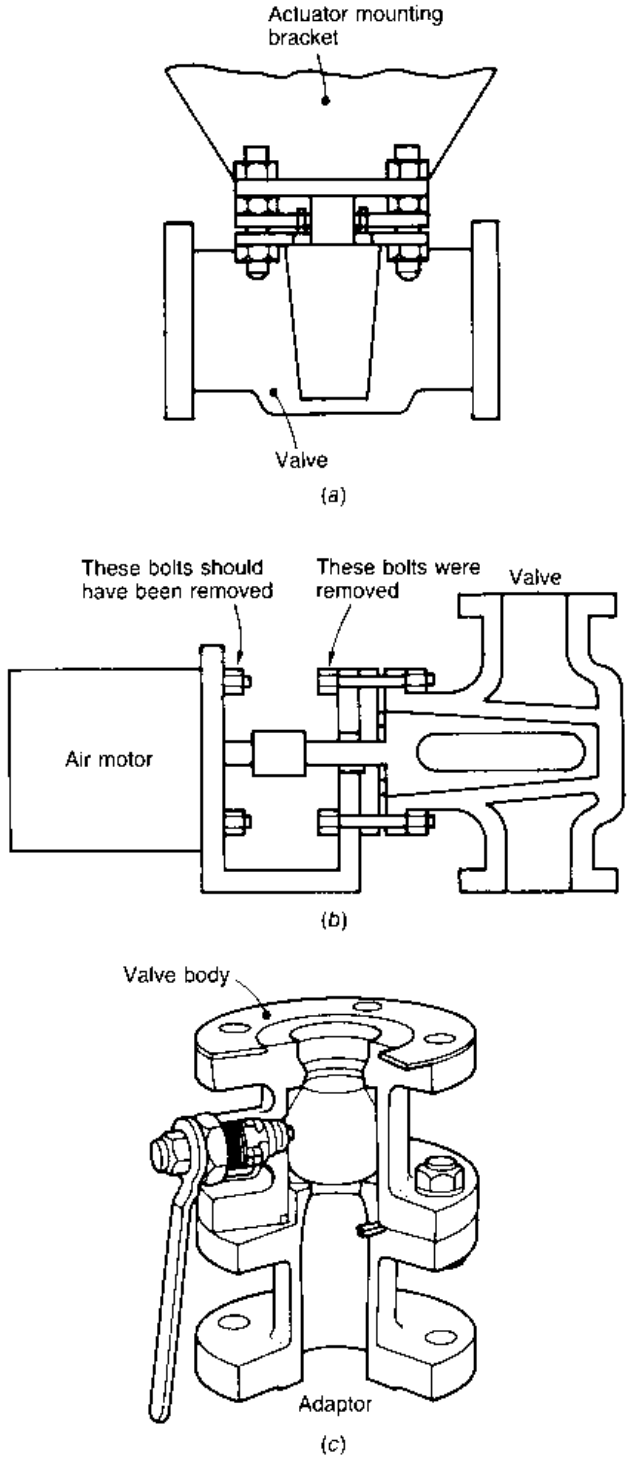


Figure 21.6 *Some valve types involved in joint breaking incidents (Kletz, 1984l): (a) valve and actuator, held by same bolts; (b) valve and actuator, held by separate bolts; (c) valve with adaptor an integral part of valve (Courtesy of the Institution of Chemical Engineers)*

opposite one was tried and also snapped. A third one was attempted but broke also, whereupon the fourth stud sheared. The single isolation, which had been tested and was thought to be good, did not prevent a release of liquid.

Alter breaking, a pipe is sometimes found to be choked. The blockage may be removed by means such as digging it out. It is not good practice to clear blockages by using air or gas pressure. The danger here is that the plug of material will be ejected as a projectile.

After breaking, the ends of pipes on the installation should be blanked off.

21.10.3 Breaking joints on valves

A particular hazard occurs on certain types of valve, where a joint containing the process fluid is liable to be broken in error. An account of this hazard is given by Kletz (1982f, 1984l).

Some situations where this hazard has been realized are shown in Figure 21.6. In the incident on the valve shown in Figure 21.6(a), the fitter was required to remove the valve actuator, secured on a stud which also held in place the valve bonnet; the latter was removed by mistake. Figure 21.6(b) illustrates the valve involved in another incident. In this case it was intended that the air motor should be removed, but the joint on the valve itself was undone. In the third incident, on the valve shown in Figure 21.6(c), the fitter removed a piece which he thought was an adaptor but which was in fact a integral part of the valve itself.

21.11 Hot Work

Hot work such as welding and cutting is a common activity on process plant, but involves potential hazards both to plant and personnel, and needs to be closely controlled. Guidance on hot work is given in HS(G) 5 *Hot Work* (HSE, 1979) (the HSE *Hot Work Guide*). Also relevant is NFPA 51B: 1989 *Cutting and Welding Processes.* API Publ. 2201: 1985 *Procedures for Welding or Hot Tapping on Equipment Containing Flammables* is no longer listed, current guidance being given in API RP 1107: 1991 *Pipeline Maintenance Welding Practices.*

The HSE *Hot Work Guide* deals with hot work operations under the following headings: (1) general principles, (2) environment, (3) equipment, (4) methods, (5) operations in buildings, (6) limitation of operations, (7) prohibited operations, (8) welding technology, (9) control of operations and (10) procedure. It includes appendices on the regulatory requirements, various types of seal plug, welding on water-sealed and waterless gas holders, and flammable gas detectors.

The *Guide* deals particularly with welding operations on plants containing flammable fluids, which is also the aspect of hot work of principal concern here. The welding should be confined to manual electric arc methods.

The welding methods described in the *Guide* require for their safe performance strict adherence to the procedures laid down. The account given here draws on the *Guide*, but is no more than an outline. The *Guide* itself should be consulted for the conduct of such welding operations.

Welding as such is treated in Chapter 12 and the personal safety aspects of welding are discussed in Chapter 25.

21.11.1 Regulatory requirements

Welding operations are covered by Section 31(4) of the Factories Act 1961, which states:

> No plant, tank or vessel which contains or has contained any explosive or inflammable substance shall be subjected
> (a) to any welding, brazing or soldering operation;
> (b) to any cutting operation which involves the application of heat;
> (c) to any operation involving the application of heat for the purpose of taking apart or removing the plant, tank or vessel or any part of it;
> until all practicable steps have been taken to remove the substance and any fumes arising from it, or to render them non-explosive or non-inflammable; and if any plant, tank or vessel has been subjected to any such operation, no explosive or inflammable substance shall be allowed to enter the plant, tank or vessel until the metal has cooled sufficiently to prevent any risk of igniting the substance.

Section 31(5) provides that, where he is satisfied that compliance is unnecessary or impracticable, the Chief Inspector may grant exemption from any of the above requirements by the issue of a certificate, which may contain conditions.

21.11.2 Control of welding operations

The welding operations should be controlled by a permit-to-work system. The general arrangements of a permit system are described in Section 21.8, but certain points of particular relevance to welding merit mention.

The issuing authority should have both the knowledge required to appreciate the hazards of the work and the precautions to be taken and the authority necessary to draw on and co-ordinate specialist expertise. The permit should specify clearly and in detail the equipment on which the work is to be done, the precise nature of the operation and the weld point. The issuing authority should inspect the work site to ensure that all necessary precautions are in place. A full explanation of the work, the hazards and the precautions to be taken is particularly necessary where the work is to be done by contractors.

21.11.3 Precautions for welding operations

A principal hazard of welding is that it introduces a source of ignition. If the work is to be done at a location where this fact is significant, and particularly within a classified hazardous area where sources of ignition are normally excluded, this should be entered on the permit and special precautions taken.

The welding site should be free of flammables, whether gases, liquids or solids. The atmosphere to a radius of 15 m and to a height of 2 m above ground level or above the point at which welding is to be done, whichever is the greater, should be free of flammable gas. The surfaces of the surrounding plant should be free of flammable deposits. There should be no flammable liquids on the ground within a radius of

15 m. Drains over the same area should be sealed. It may also be necessary to provide shielding to contain weld spatter.

The equipment to be worked on should normally be isolated, emptied and cleaned, tested for flammables and inspected before welding is undertaken. There are certain procedures which are exceptions, as described below, but they in no way weaken this general rule.

There should be good access to the welding site for the welders and equipment and also for emergency services. For elevated locations, suitable staging and scaffolding should be provided, again with good access. There should be adequate lighting. For welding on underground pipelines an excavation should be made of sufficient size, with adequate shoring, ladder access and secondary means of escape.

For welding in any confined space, including an excavation, there should be ventilation sufficient to ensure dispersion of fumes.

Suitable protective clothing should be provided for all persons involved in the welding operation. There should be present as a 'fire watch' at least one person, who should be provided with fire extinguishers, the dry powder type being generally used. First aid equipment such as breathing apparatus and resuscitation equipment should be to hand.

Personal safety in welding operations is considered in Chapter 25.

21.11.4 Welding on plant containing flammable fluids

The conditions under which welding may be carried out on plant containing flammable fluids are defined in the HSE *Hot Work Guide*.

For welding on the external surface of plant containing a flammable liquid, the metal at the location of the weld should be wetted by liquid. For welding on the external surface of a tank the weld should be below the liquid level and for welding on a pipeline the pipeline should be full of liquid. In the latter case it is also necessary to ensure that abnormal pressures cannot arise due to the generation of vapour or expansion of the liquid. The usual method of avoiding this is to maintain a liquid flow that is high enough to prevent overheating but not so high as to cause overcooling; a liquid velocity of at least 1 m/s is usually required. Measures should be taken to ensure that penetration of the metal does not occur. These include ensuring that the thickness of the metal in the area of the weld is sufficient and that the welding is performed properly.

Where welding is to be done on the internal surface of plant which has contained a flammable liquid, precautions should be taken to ensure that the surfaces are free of deposits and that no liquid is trapped in hollow members or behind metal linings or wear plates. Trapped liquid should be released by drilling suitable holes and the space purged with steam, air or inert gas, as appropriate.

Welding on the plant containing a flammable gas involves a higher potential hazard in that gas has a much lower capacity for the removal of heat than does liquid. There is thus a greater risk of overheating which may result in penetration by the welding operation or rupture due to the internal pressure. The operating pressure and temperature should be adjusted to allow for this.

21.11.5 Methods of temporary isolation

Some of the welding operations described below require the temporary isolation of a section of pipe. Where possible isolation should be effected by conventional means, but in some cases it is necessary to use seal plugs or bag seals.

Four types of seal are described in the HSE *Hot Work Guide*, which devotes an appendix to each. These are (1) atmospheric seal plugs, (2) high pressure seal plugs, (3) frozen product seal plugs and (4) bag seals.

An atmospheric seal plug is inserted into the open end of a pipe which has been isolated by other means, drained and cold cut, but which has not been cleaned along its entire length and into which flammable liquid or gas may leak. It consists of a rubber sealing ring compressed between two discs so as to provide a peripheral seal against the inside of the pipe. It provides an isolation between the welding point and the empty line.

A high pressure seal plug is inserted into an operating pipeline, using a seal plug insertion unit. There are a number of designs of such seal plugs. The insertion of two high pressure seal plugs allows a section of pipe to be isolated.

A frozen product seal plug is created by freezing the liquid in a section of the line, using a freezing mixture, commonly of solid carbon dioxide and isopropanol. Where the liquid cannot be frozen in this way, it may be possible to use the alternative method of replacing it with water which can then be frozen.

A bag seal is inserted into an operating gas pipeline through a bag tube. The bag consists of an inflatable rubber bladder with an outer fabric cover. Bag seals are used only for pipelines containing gases at low pressure.

Full details of each of these seal methods, of their applicability and limitations, and of the precautions to be taken in their use are given in the HSE *Hot Work Guide*.

21.11.6 Welding on operating pipelines

The HSE *Hot Work Guide* describes the method to be followed in welding operations on pipelines carrying flammable fluids. The *Guide* deals primarily with welding on a pipeline for the purpose of replacing a length of pipe. It treats both the case where the pipeline has to remain in operation and that where it can be taken out of service.

For the former case, the method described is to isolate the section of pipeline on either side of the pipe section to be replaced. If the isolations cannot be effected by conventional means, use may be made of a suitable seal plug. This will often be a high pressure seal plug. The method of inserting such a seal plug is broadly as follows. A stub connection is welded to the pipeline, a special valve is mounted on the connection and the drill is mounted on the valve. A check is made to ensure that the fitments and welds can withstand the pipeline pressure. The valve is then opened, the drilling is done, the drill is withdrawn again, the valve is closed and the drill is removed. The seal plug insertion unit is fitted and the seal plug inserted. If the flow is to be maintained, this may be done by putting in first a temporary bypass, again by welding on stub connections and tapping in a similar manner, and joining the bypass pipe on by a flanged or welded joint. Further stubs are welded on to the pipe section to take vent and drain

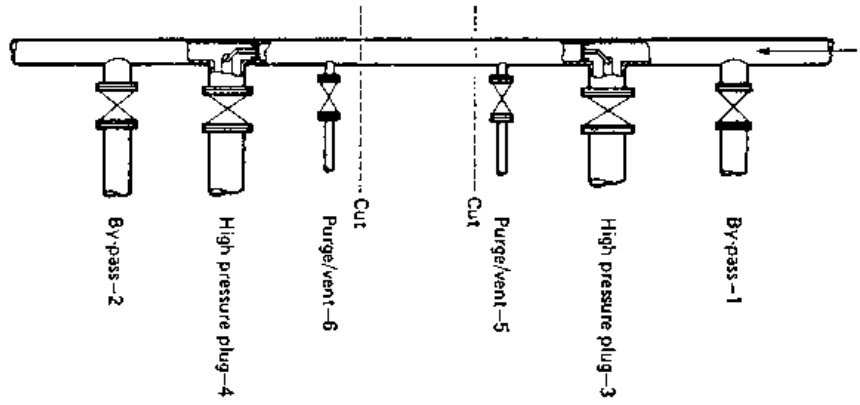


Figure 21.7 *Arrangement for welding on an operating pipeline (HSE, 1979 HS(G) 5) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

connections and these are tapped. The arrangement is illustrated in Figure 21.7. The pipe section is drained and vented and a check is made that the seal plugs are making satisfactory seals. The pipe section is then removed, which should be done by cold cutting; this does not include the use of an abrasive wheel. The pipe ends are cleaned and the new section of pipe is then fitted, either with flanged or welded joints. If there is to be a delay before the pipe section is fitted, the open ends should be sealed with atmospheric seal plugs or bag seals and the space behind these seals vented by flexible hose to a safe area.

A permanent branch connection may be fitted to an operating pipeline in a manner essentially similar to that just described for the fitting of a temporary bypass, and a valve or flowmeter may be fitted in a manner similar to that described for the fitting of a new section of pipe.

Another case is where the pipeline can be taken out of service and the section of pipeline isolated and drained, but it is not practical to clean and purge it over its whole length. In this case the isolations should be checked and the line drilled to ensure it is depressurized to atmospheric pressure. The pipe section is then removed by cold cutting. As before, the pipe ends are cleaned and the new section of pipe is then installed, with fitting of seals and venting of the space behind them if installation of the new pipe section is to be delayed.

Yet another case is where it is necessary to effect a repair on an operating pipeline to counter internal or external corrosion. It is sometimes possible to use a mechanical clamp, but often the only recourse is to weld over the affected area a patch or leak box. The *Guide* gives details of the procedure to be followed.

21.11.7 Limitations and prohibitions on welding operations

The HSE *Hot Work Guide* sets a number of limitations on the welding operations described on plant containing flammable fluids. Welding should not generally be carried out on plant where the metal thickness is less than 5 mm; on the external surface of a tank at a point less than 1 m below the liquid surface, or on plant at a temperature below 7°C, unless it can be shown to be safe to do so.

Welding on a pipeline should not be undertaken where the operating pressure and temperature exceed those which ensure that the thickness and strength of the metal are such as to preclude failure and that the strength remains unaffected on cooling.

Welding should not be done on the vent and blowdown systems of operating equipment, unless it can be shown to be sale to do so. Such systems should not be isolated whilst the plant is operating unless alternative arrangements have been made.

There are also a number of prohibitions on welding operations on plant containing flammable fluids. Welding should not be carried out where: either the plant contains a flammable mixture or the welding itself may create one; the plant contains a substance liable to undergo reaction or decomposition; or the plant contains either compressed air or an oxygen-enriched mixture together with hydrocarbons deposited on internal surfaces or otherwise present.

Furthermore, welding should not be carried out on: plant in ferritic steel containing gas in which the partial pressure of hydrogen exceeds 7 bar, unless it can be shown by tests to be safe to do so; plant in a material liable to stress corrosion cracking, unless appropriate stress relief treatment can be given; plant for which post-weld heat treatment is necessary; plant designed to advanced, or high stress, codes; or any part of a flare system over which effective control cannot be exercised.

The *Guide* draws attention to the extreme hazard of welding on plant containing pure liquid or gaseous oxygen. For plant containing high purity ethylene gas it notes that at the time of writing it had been demonstrated that welding may be safely done at pressures up to 28 bar and temperatures up to 150°C and that work was continuing on this topic.

21.11.8 Procedures for welding operations

The HSE *Hot Work Guide* gives the procedures to be followed in welding operations on a pipeline in the form of a checklist, under the headings of: (1) initial planning of operations, (2) site preparations, (3) stand-by services, (4) pipeline preparation, (5) fitting alignment, (6) welding procedure, (7) action immediately prior to welding, (8)

action during welding, (9) integrity of the completed weld and (10) final completion.

The initial planning covers: checks on regulatory requirements and company codes; notifications to external interested parties; reviews of the process conditions, of the condition the pipeline, of the fittings and consumables, and of the site conditions; lists of the fittings, equipment, and services required, plans of the site; sketches of the work; a list and plan of emergency procedures; and preparation for the issue of the permit. The site preparations are essentially the precautions given in Section 21.11.3, but include also the provision of adequate supports for the pipeline, fittings and any other equipment, and removal of groundwater where necessary. likewise, the stand-by services to be provided as appropriate are those mentioned in that section.

The pipeline preparations include checking the material of construction of the pipeline, removing insulation, cleaning the surface, checking the ovailty, measuring the wall thickness, examining the external condition, investigating where necessary the internal condition, and grinding flush any external weld which might interfere with a flush fitting.

The fittings alignment requires that the fittings be correctly positioned and aligned, the pipeline and fittings adequately supported, and the weld preparation and the clearances checked. The welding procedures cover the competence and approval testing of welders, the routing of the welding cables though areas free of flammable gases and liquids, the condition of these cables, and the clamping of the return current cable close to the weld point.

The actions immediately prior to welding are to confirm the identity of the pipeline to be welded, the pipeline operating conditions, the welder and welding supervisor's understanding of the work to be done, the temperature of the pipe wall and fitting, the welding current, and compliance with the permit. The actions during welding are to monitor the pipeline operating conditions and the absence of flammables in the environment.

The integrity of the completed weld should be such that it is able to withstand any operating conditions to which the pipeline may be subject, after heat treatment where necessary. The integrity of the weld should be checked by some suitable means. Reference is made to hydraulic pressure testing, pneumatic leak testing and non-destructive testing. Where the latter is used the acceptance standards utilized should be stated. Where pressure testing is used, care should be taken to avoid overpressurizing the pipeline itself.

The final completion consists of the usual termination procedures: a check that the site is left free of hazards, notification to interested parties that the work is complete, and cancellation of the permit.

21.11.9 Hot tapping

The procedure of fitting a branch onto a pipeline which is still operational is known as hot tapping. This procedure has already been described in outline but is of sufficient importance to merit further discussion. As already stated, guidance is available in the HSE *Hot Work Guide*. Further guidance is given in API RP 1107: 1991.

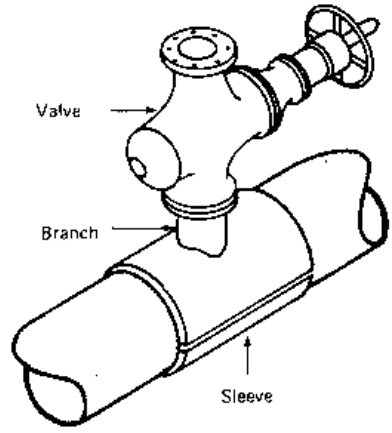


Figure 21.8 *Valves arrangement for hot tapping*

Several of the accounts on hot tapping published in the mid-1970s provide useful background information. They include those of Elder and Batten (1975), Hahn (1975), W.B. Howard (1975a), Howden (1975), Letchford (1975) and Warren (1975a). Howden (1975) describes a long-term programme of work on hot tapping in the American Gas Association (AGA) Line Pipe Research programme at the Battelle Columbus Laboratories. Guidelines produced by the American Society of Mechanical Engineers (ASME) Gas Piping Standards Committee are outlined by Elder and Batten (1975). The development of a code of practice for hot tapping has been described by Letchford (1975) of British Gas. There are guidelines developed by the British Pipeline Industries Guild.

It is expensive to shut plant down and there is a strong economic incentive to make the modification with the plant working. Nevertheless, hot tapping should be avoided as far as possible and should only be done in essential cases.

The Factories Act 1961, Section 31(4), quoted above, forbids work on plant, tanks or vessels containing any explosive or flammable substance which entails the application of heat until all practicable steps have been taken to remove the substance and any fumes arising from it and to render it non-explosive or non-flammable.

If air or other oxidizing substance is excluded from plant which contains a fluid that can burn or explode when mixed with air, then the fluid may be regarded as non-explosive and non-flammable. Such exclusion is the basis for the justification of hot tapping as an industrial practice (Hahn, 1975).

There are several hazards in hot tapping. One is that there will be a leak during the hot tapping operation itself. This is most likely to result from welding, but could also occur if the hot tap valve or tapping machine were to fail or if the tapping machine were to pierce the pipe on the far side. Another hazard is the explosive decomposition of the fluid in the pipe due to the heat applied during the welding. A third hazard is the failure of the modified plant at some later date. There are also the usual hazards of welding on the plant.

The normal hot tapping arrangement is shown in Figure 21.8. A branch is welded onto the pipe, a valve is put on the branch and a tapping machine is used to drill via the valve and branch into the pipe.

Hot tapping requires careful preparation, including consideration of the following factors:

(1) the process fluid and the process design operating conditions in the pipeline;
(2) the process operating conditions at the start of work;
(3) the material of construction, the dimensions and the condition of the pipeline;
(4) welding constraints, preparations and procedures;
(5) the fittings and equipment required for the work;
(6) the services required for the work;
(7) the plant operational procedures and precautions;
(8) the permit systems, notification to third parties, and emergency arrangements.

If possible, the pipeline should be taken out of service to make the hot tap. Where this cannot be done, the operating pressure above atmospheric should be reduced as far as possible while the work is being done so that the hazard is also reduced.

The material of construction, the thickness and the condition of the pipe to be welded should be thoroughly checked. The material of construction is important for strength calculations and for the selection of welding electrodes. There is a minimum thickness below which the pipe should not be welded. Welding should not be carried out if the condition of the pipe has deteriorated so as to make operation unsafe, and the pipeline should be thoroughly checked by non-destructive testing (NDT).

Some guidelines on what is and what is not permitted in one company, ICI, have been given by Hahn (1975). Basically, these restrict hot tapping to the following conditions:

(1) pipelines to be made of specified grades of steel;
(2) pipe wall thickness to be not less than 022 in.;
(3) process fluid pressure to be not greater than 550 psig and not less than atmospheric; if hydrogen is present, the partial pressure to be not greater than 100 psig;
(4) process fluid temperature to be between 7°C and 370°C throughout the operation; preheating by steam or electrical methods, but not flame heating, to be used as necessary to achieve this;
(5) welding not to be done on lines containing—
    (a) oxygen (except under 1%),
    (b) compressed air,
    (c) decomposables,
    (d) caustic soda,
    (e) process materials which could cause hardening by reaction with hot metals to a dangerous degree.

Hahn also discusses the extent to which these basic restrictions can be modified and states the conditions under which his company would do hot tapping on low alloy steels, on thinner pipes, at higher pressures and outside the given temperature range. On the other hand, he also gives certain limits which would not be overridden: welding would not be done on oxygen or chlorine pipes, because steel can burn in these materials, nor on compressed air lines, which often contain oil or carbon deposits that might ignite if heat were applied to the pipe. Areas of doubt which he discusses are pipelines containing ethylene and those containing hydrogen above 100 psig partial pressure.

The problem of ethylene decomposition during welding on ethylene pipelines is considered by W.B. Howard (1975a), who describes experiments to determine the process conditions under which hot tapping may be regarded as safe. Hahn states that his company has gone from a policy of permitting such work to a complete ban and thence to a partial relaxation of the ban. It is of interest that during the period of the complete ban a method was developed for bonding fittings in place using epoxy resins.

With regard to hydrogen, Hahn suggests that the hazard which is a greater limitation than that associated with hydrogen partial pressure is that the red hot part of the heat-affected zone may reach the pipe internal surface with the result that the hydrogen diffuses rapidly through the weld pool, so that weld cracking occurs.

The welding work has several important aspects. The welding is done by the electric arc method. The welding procedure should be defined in respect of the electrode selection, the welding technique, the preheat and the post-weld treatment, if any.

Preheat may be provided by steam or electrical methods. Different views have been expressed on the advisability of flame heating. The ICI instructions described by Hahn state that it should on no account be used. On the other hand, Letchford describes its use in British Gas.

The surfaces to be welded should be uniform and free of pipe coating, rust, scale, oil and moisture. The pipe should be supported on both sides of the section to be welded.

The welding current should be checked. The ammeter on the welding set is not always reliable. It is usually required that the meter be checked using scrap material. The pipe should be completely earthed and the risk of arcing at the earth clamp eliminated.

The welders should be fully qualified, experienced and reliable men, and should wear appropriate protective clothing.

If the weather conditions are bad, the welding should be stopped.

There can be a significant cooling effect from the gas flow. This may require the use of higher welding current to overcome this cooling effect. It can also result in cracking due to the quench effect when the source of heat is removed.

The hot tap valve requires special attention. Such a valve may be subjected to pressure and temperature shocks and its integrity should be assured. The valve should be new. It should be given NDT, pressure and leak tests.

The hot tapping equipment should also be carefully checked. This check should again include NDT and pressure testing and tests on the cutter teeth and pilot drive.

The plant operational procedures and precautions which should be taken during hot tapping were described in Chapter 20 as an illustration of the role of plant management during plant engineering work.

Hot tapping is a complex operation which is potentially hazardous, but which can be done safely if the correct practices are followed. The foregoing account does no

more than outline the general nature of the operation and some of the problems. It is emphasized, however, that hot tapping is a matter for specialists.

21.12 Tank Cleaning, Repair and Demolition

A set of operations of some importance in the maintenance of plant is the cleaning, repair and demolition of tanks for storage of flammable liquids. Guidance is given in CS 15 *The Cleaning and Gas Freeing of Tanks Containing Flammable Residues* (HSE, 1985). This supersedes guidance given previously in TDN 18 *The Safe Cleaning, Repair and Demolition of Large Tanks for Storing Flammable Liquids* (HSE, 1975). Also relevant is NFPA 327: 1987 *Cleaning or Safeguarding Small Tanks and Containers*.

CS 15 applies to land-based tanks, but not ships' tanks, and to flammable liquids, but not liquefied gases such as LPG. It distinguishes the following types of container: (1) small tanks (capacity $< 60\ m^3$), drums and other small containers; (2) mobile tanks; and (3) large tanks. The tanks described are those where the liquid products are flammable rather than toxic, though they may in some cases be both.

TDN 18 treats four cases in the repair and demolition of tanks: (1) tank repair, liquid flashpoint $< 38^\circ C$; (2) tank demolition, liquid flashpoint $< 38^\circ C$; (3) tank repair, liquid flash point $> 38^\circ C$; and (4) tank demolition, liquid flashpoint $> 38^\circ C$. There is no such explicit classification in CS 15.

21.12.1 Preparation for entry or hot work

Two principal purposes for which entry into a tank is required are inspection and repair or modification, which usually involves hot work.

It cannot be assumed that a tank which has been emptied and gas freed, or even one which has been cleaned with a water wash, is completely free of flammable or toxic gas. Before entry, ventilation of the tank should be established, the atmosphere should be shown by a gas test to be free of flammable or toxic gas, and repeat gas tests should be made at intervals to confirm that the atmosphere is still gas free. On entry, a check should be made for potentially hazardous residues.

If it is not possible to establish a safe atmosphere in the tank, entry may be made using breathing apparatus. Ventilation and monitoring of the atmosphere in the tank should continue and personnel should not remain inside if the concentration of flammables rises to over 25% of the lower flammability limit.

Before hot work is undertaken, a thorough inspection should be made for hazardous residues and any such residues first removed by cleaning.

It may be possible, particularly for smaller tanks, to avoid the need for hot work by cold repair techniques such as the use, where suitable, of materials based on epoxy resins, fibre glass or elastomers. Care should be taken not to incorporate into the tank structure elements which increase the hazard from static electricity.

21.12.2 Gas freeing of tanks

Methods of gas freeing are described in Section 21.6. They are forced ventilation, water washing and steam cleaning. Particularly with large tanks, the gas freeing or cleaning operation may involve the venting of quantities of flammable or toxic vapour, which is often denser than air, and therefore liable to collect at low points and poorly ventilated areas. Such operations should not be performed unless suitable precautions have been taken to disperse the gas and exclude ignition sources.

In some cases the operations will evolve quantities of flammable vapour sufficient to require measures to control its dispersion. Flammable purge gas mixture is sometimes burned off at an elevated vent stack, fitted with a pilot flame and a flame arrester to prevent flashback. Where large tanks, and therefore large volumes of flammable vapour, are involved, the dispersion of the vapour should be monitored, by measurement if necessary, and venting suspended if the vapour fails to disperse. Other precautions required include the sealing off of drains and sewers to prevent ingress of vapours and restriction of access to the area. It may also be necessary to take measures to prevent ingress of vapour into buildings.

21.12.3 Emptying of liquid from tanks

Liquid should be emptied into a suitable receiver. Large tanks are pumped out, whilst small vessels may often in inverted and left to drain.

A particular technique used to flush out light hydrocarbons from a tank bottom is to introduce water and raise the hydrocarbons to the level of the suction line so that they can be pumped out. Care is needed to avoid generating static electricity either by high fluid velocities or by splashing, bearing in mind the enhancing effect of the water content on the generation of static electricity in liquid hydrocarbons.

Where a vessel has an external jacket for the circulation of a flammable heat transfer liquid, it is suggested in CS 15 that this may be drained out and replaced with water, maintaining a vent open to the atmosphere to prevent any pressure build-up during hot work.

Suitable measures should be taken to ensure that ancillary equipment does not constitute a hazard. Ionizing radiation sources should be removed by a competent person. Stirrers and heaters should be isolated. Cathodic protection should have its power supply isolated 12 hours in advance so that depolarization occurs. Where it is necessary to maintain heating from steam coils or an electric immersion heater in order to assist pumping out of the liquid, the heat input should be isolated before the liquid falls to within 0.5 m of the heating surfaces or temperature sensors.

21.12.4 Ignition at tanks

Precautions should be taken to ensure that ignition of flammables does not occur. The main precautions are the elimination of a flammable mixture and the avoidance of hot work where there may be flammable residues; but where there are flammables which might be ignited, control of ignition sources should be exercised. Ignition sources and situations which are particularly relevant to tanks are: direct flames from hot work; hot surfaces occurring due to hot work; self-heating of oil-soaked lagging; and pyrophoric iron sulphide. Hot surfaces may cause ignition either by hot surface ignition or by raising the temperature of the bulk gas to its autoignition temperature. There is a volume effect for autoignition, the autoignition temperature decreasing with an increase

in volume, and since the volume differences are large between the volumes in which determinations have been made and those of large tanks, it is prudent to assume that any significant rise in the wall temperature may ignite a flammable mixture in a large tank.

21.12.5 Gas freeing and cleaning of small tanks

For small tanks, drums and other small containers, use should be made of positive gas freeing methods and reliance should not be placed on natural ventilation. One positive method of gas freeing is forced ventilation. Gas freeing also occurs as a result of cleaning by water washing or steam cleaning.

Methods of cleaning small tanks are water washing, steam cleaning and solvent jetting. An account of the use of these methods for the cleaning of small tanks is given in Section 21.6.

21.12.6 Gas freeing and cleaning of mobile tanks

Mobile tanks are those on road tankers and rail tank cars. Positive methods should be used for gas freeing. One such method is thorough water washing and forced ventilation by the use of an air eductor or air mover. Another is to do gas freeing as part of steam cleaning. The usual method of cleaning, and thus of gas freeing, is the use of steam cleaning. The procedure is similar to that for small tanks.

Before hot work is undertaken on a multi-compartment tank vehicle, the design of the tank should be reviewed and a check made that there is no flammable material trapped in the bulkheads or other cavity.

21.12.7 Gas freeing and cleaning of large tanks

The usual method of gas freeing a large tank is by forced ventilation using devices such as air eductors or air movers. The eductor or blower trunking is lowered to the tank bottom and the tank is freed of gas through the roof manholes. The opening of manholes in the side of the tank may release dense vapour creating a potential hazard, as described above. Precautions should be taken against ignition.

Ventilation should be continued until the concentration of vapour falls to less than 5% of the lower flammability limit. At this point the risk of an outflow of flammable mixture is minimal and all the manholes may be opened. The flammable concentration should be allowed to fall to zero and to stay there for at least 30 minutes.

Methods of cleaning large tanks are steam cleaning, water jetting, solvent jetting and manual cleaning. An account of the use of these methods for the cleaning of large tanks is given in Section 21.6.

CS 15 describes additional measures to be taken with floating roof tanks and fixed roof tanks with floating covers.

In many cases, the bottoms of large tanks are covered with sludge, residues and corrosion products, and are perforated to some degree. There may be hazardous residues in defective seams or in voids. It is necessary to check on, and deal with, such residues before hot work is undertaken.

Relevant advice is given in API Publ. 2207: 1991 *Preparing Tank Bottoms for Hot Work*. If there is flammable liquid under the tank bottom, one technique of dealing with it is to drill and flood the bottom with water to displace the liquid.

21.12.8 Hot work on outside of tanks

If it is required to carry out hot work on the outside of a tank which for some reason cannot be gas freed and cleaned, an alternative procedure is to inert the tank. This method is not suitable if the product concerned is one which decomposes, such as ethylene oxide. Another procedure is to fill the tank with the flammable liquid and then perform the hot work, as described in Section 21.11.

21.12.9 Inerting of tanks

Inerting may be effected by filling with water or with an inert gas such as nitrogen, carbon dioxide or combustion gas. A simple method of inerting for small tanks is filling with water. Any necessary check should be made on the load created by the water on the tank and its supports.

The inert gas method requires that the gas be mixed effectively. Mixing is promoted by the introduction of the inert gas at a number of points and with high velocity. Failure to achieve good mixing creates various problems. It is difficult to monitor the uniformity of mixing and it may be necessary to maintain the gas flow throughout the period of the hot work.

Nitrogen is less reactive than carbon dioxide and may be used where products might be adversely affected by the latter. It is available as compressed gas in cylinders or as the bulk liquid. Where the latter is used, the vaporizers should be large enough to ensure an adequate supply and should be able to warm the gas to at least $-10^{\circ}C$ to guard against low temperature embrittlement. Using nitrogen inerting, which gives a mixture of hydrocarbons, nitrogen and oxygen, the limiting concentration of oxygen for combustion is about 12% and it is usual to purge down to below 5% to allow an adequate safety margin.

As just stated, carbon dioxide is more reactive than nitrogen. It too is available as compressed gas in cylinders or as the bulk liquid. Carbon dioxide has a tendency to form solid particles. In the case of cylinders this creates a risk from static electricity, and CS 15 advises against the use of the cylinder gas for this reason. Discharge from the bulk liquid should be designed to prevent the formation of 'snow'. It should be checked that the tank can withstand the low temperature caused by liquid or solid carbon dioxide. Precautions should be taken to protect personnel from 'cold burns'. Using carbon dioxide inerting, the limiting concentration of oxygen for combustion is about 14%, and for safety it is usual to purge to below 5%.

A third type of inert gas is combustion gas obtained from the controlled combustion of hydrocarbons in gas generators, followed by purification. The resultant mixture typically contains 12–15% carbon dioxide, 12% oxygen and the remainder nitrogen.

Another inerting technique involves the use of foam. The foam may be an air foam or a nitrogen foam. High expansion foam blown with air has been used to inert tanks which have held high flashpoint liquids, but there is some doubt whether air foam will prevent flame propagation if vapour is evolved in any quantity and it should not be used for liquids with a low flashpoint ($<32^{\circ}C$). Instead use may be made of nitrogen foam. The principal advantage of using nitrogen in foam form is economy in the use of the gas, since the gas in the tank is displaced by the foam rather than removed by

effecting a number of purge gas changes. CS 15 gives detailed procedures for the use of nitrogen foam and for hot work using it.

21.12.10 Demolition of tanks

Methods for the demolition of tanks are given in GS 29/3 *Health and Safety in Demolition Work. Part 3: Techniques* (HSE, 1984). This supersedes guidance given previously in TDN 18 *The Safe Cleaning, Repair and Demolition of Large Tanks for Storing Flammable Liquids* (HSE, 1975).

A demolition survey should be made and the demolition procedures defined. The tank should be emptied and gas freed. Ignition sources should be controlled. The roof should be removed by cold cutting. If a power tool is used, precautions should be taken to avoid its acting as an ignition source, suitable measures being suggested in GS 29/3. Before any hot work is done, the tank should be cleaned from the outside, by use of steam hoses, washing with water or water sprays. Washing with a high flashpoint oil is another method, but the oil should not be sprayed. The wash fluid should be pumped away.

If steam is used, the usual precautions should be taken, the steam pipe being earthed and bonded to the tank. The tank should be allowed to cool and the atmosphere tested before entry is made.

In some cases the technique is used of covering the bottom sludge with about 0.15 m of water.

Further details of tank demolition are given GS 29/3, which also describes specific methods for the demolition of various types of tank, including small and large fixed roof tanks, floating roof tanks, and leaded petroleum tanks. It also deals with tank walls and tank floors.

21.13 On-line Repairs

There has been a steady growth in the development of techniques for on-line, or on-steam, repair and in their application. An account of on-line repair methods in general is given by G.W. Harrison (1980).

The growth of such techniques has been driven by a number of factors, including general economic pressures and the needs to accommodate the lengthening of times between scheduled shut-downs, or turnarounds; to keep major pipelines operating; to economize on energy and reduce steam leaks; and to reduce hydrocarbon emissions.

One family of on-line repair methods is that concerned with carrying out hot work on operating pipelines, including hot tapping. This has already been described in Section 21.11.

Among the applications of on-line repair described by Harrison are the use of: drill-and-tap methods to repair packings on leaking valves and also on pumps and agitators; leak sealing methods to eliminate flanged joint leaks, piping and fitting leaks, vessel leaks and compressor and turbine case joint leaks; hot tapping and line stopping on pipelines; various leak sealing methods for heat exchangers; and the crimping of deteriorated reformer tubes.

An account of on-line repair of insulation is given by Bloom and Pebworth (1979).

21.13.1 General leak sealing

One of the most common types of on-line repair is the sealing of a leak. A variety of simple methods are used to seal leaks such as steam leaks, including clamps and various forms of enclosure or box. These may often be applied without the need to weld on an operating pipeline.

21.13.2 Compound leak sealing

A specialized leak repair technique is that of on-line compound leak sealing. One of the main points on a plant where a leak is liable to occur is at a flanged joint. If the leak is sufficiently severe, there may be no choice but to shut down and repair it, unless it can be repaired on line with the plant still operating. Accounts of compound leak sealing are given by Stroud (1981), Maushagen (1984 LPB 55), Bond (1986 LPB 69) and J.K. Rogers (1988).

Compound leak sealing of a flanged joint involves putting a containment around the joint and injecting a sealant under pressure. J.K. Rogers (1988) describes the Furmanite system of leak sealing. This is applicable over the pressure range 100 mbar vacuum to 350 bar and the temperature range −30°C to 600°C. A family of sealing compounds is used, depending on the application. The applications quoted are not only to flanged joints on pipes but to various other types of equipment, including riveted joints, welded joints, screwed couplings, valves and heat exchangers.

An investigation of the hazards associated with this technique is described by Maushagen (1984 LPB 55). In essence, the process of leak sealing tends to lead to an increase in the stress on the flange and on the bolts. There is thus a potential hazard of rupture at the flange, which is particularly likely to be realized if the flange assembly has a burst pressure below the nominal value due to incorrect design, incorrect materials or deterioration. The author defines a factor relating the stress on the bolts after sealing to that on the bolts as installed, and quotes values of up to 2 for this factor. Each application needs, therefore, to be assessed before sealing is undertaken.

He also describes a number of case histories of flange rupture during leak sealing. In one case in Czechoslovakia in 1981, a 300 mm diameter pipe at 300 bar pressure containing synthesis gas for an ammonia plant developed a leak at a lens ring joint. A leak sealing operation was undertaken by non-specialists. During the injection of the sealant there was a massive failure of the flange, resulting in a fire and explosion which killed four people.

Further leak sealing incidents are described by Bond (1986 LPB 69). Nevertheless, he argues that leak sealing is not a particularly risky operation. In the UK some 25 000 leaks are sealed each year by some 100 technicians.

Bond outlines the precautions required to minimize the risks of leak sealing. Where possible, it is preferable to use conventional means of repair, such as repair or renewal of components, rejointing of flanges and repacking of glands.

If leak sealing is to be undertaken, it should be assessed by a competent engineer and a formal work programme agreed, covered by a permit-to-work. The assessment should cover: the hazard of a major release;

the residual thickness of the pipe, including the method of, and apparatus for, its measurement, the bolts, including materials, deterioration, initial and final stresses; the external loads on the pipe and flange; the record of past injections; the maximum injection pressure to be used; the design codes and procedures for the boxes and clamps; the possibility of internal blockage of the pipe by the sealing compound; the access to the site; the personal protection required; and the expected life of the temporary repair. The temporary repair should be dismantled and a conventional repair effected at the earliest opportunity.

The work should be done by a competent contractor. The author highlights in particular competence in the design of boxes and clamps. Once the method to be used has been decided, no deviation should be permitted.

21.13.3 Pipeline repair

On-line repair methods have been used for many years for pipeline repair. The methods of hot tapping were developed in this application.

An account of the technique of half-soling is described by P.M. Scott and Kiefner (1984). This consists of welding to the pipeline a curved plate which is concentric with, and extends around, one-half the circumference of the pipe. The half-sole may be cold formed from steel plate or obtained by splitting a segment of pipe longitudinally, the former being the more usual. It is attached to the pipeline by a fillet weld. The technique is used both for leaking and non-leaking defects.

21.14 Maintenance of Particular Equipment

The deterioration and failure of equipment, which is dealt with by maintenance, has causes in design and installation as well as operation, and has first to be detected by inspection. The intimate links between maintenance and these other activities may be illustrated by considering the maintenance of some particular types of equipment.

Accounts of maintenance of particular equipment are given in the *Standard Plant Operators Manual* (Elonka, 1975), *Pressure Vessel Systems* (Kohan 1987) and *Plant Engineer's Reference Book* (Snow, 1991).

21.14.1 Pressure vessels

The assurance of the integrity of pressure vessels depends largely on inspection and pressure relief. For pressure vessels maintenance *per se* does not bulk large in the literature. Most accounts deal either with inspection or with incidents.

The maintenance function should maintain a general oversight of pressure vessels, with a view to detecting features such as external corrosion, support defects, stress inducing features, disabled relief protection and disabled instrumentation.

The ancillary features of a pressure vessel should be maintained in good condition. The condition and tension of the bolts on flanged joints should be correctly maintained. The relief system of the vessel should be maintained, as described below.

Where it is necessary to carry our repairs on a pressure vessel, this should be done in accordance with the appropriate codes and systems. In the UK the relevant code is BS 5500. In the USA the code is the ASME *Boiler and Pressure Vessel Code.* The National Board of Boiler and Pressure Vessel Inspectors (NB) certifies organizations for the repair of pressure vessels and issues the *National Board Inspection Code,* which gives guidance on pressure vessel repair.

Some of the problems which may occur in field repairs of pressure vessels by welding are discussed by Kohan (1987). They include: incomplete removal of the defect being repaired; increased stress and distortion; slag inclusions; undercut, overlap and incomplete joint penetration; weld porosity; weld cracks; and unfavourable access and environmental conditions.

Repairs described by Kohan include: pitting repair; repair of wasted or general corroded areas; flush-welded inserts; repair to cracks, including weld cracks and lap cracks; repairs to heat exchangers; repairs to stainless steel; and repairs to dissimilar metals.

21.14.2 Pressure relief devices

Pressure relief systems provide essential protection for pressure systems and much effort goes into their design. This is negated if the relief system is not properly maintained. Accounts of the maintenance of relief systems are given by Anon. (1977 LPB 14, p. 2; 1977 LPB 17, p. 15), Woolfolk and Sanders (1984, 1987), J.K. Rogers (1988) and Duckworth and McGregor (1989). The account by Duckworth and McGregor covers not only the maintenance of relief devices but also their installation and inspection.

The maintenance of relief devices such as pressure relief valves and bursting discs requires suitable training. Maintenance personnel need to understand the reasons for the use of such devices, the types of device, the methods of installation and the methods of testing. They should appreciate that these are delicate items of equipment and should be treated on a par with, say, instrumentation.

When installing a relief device attention should be paid to the orientation, the alignment, the gaskets and the bolt torquing. A bursting disc assembly may be rendered useless if it is incorrectly assembled, installed upside down or interfered with by an unsuitable gasket.

Before removing a relief device for testing a check should be made on its general condition to see whether it has suffered damage or interference, whether it has suffered excessive corrosion or whether there is any process fluid or deposit which could affect its operation. In the workshop checks should be made as to whether the set pressure is correct and whether there is any wear, damage, corrosion or restriction which could affect its operation. Where relapping of a relief valve seat is required, this should be done on a proprietary lapping machine or a good quality lapping plate.

A large site will generally have a large number and wide variety of types, duties and settings of pressure relief valves. There is thus considerable scope for incorrect installation. One measure to prevent this is to mark the valve location with a permanent code number and to put the same number on the valve itself.

An account of a programme for the maintenance of safety relief valves (SRVs) on a 688–acre site with 20 separate units has been given by Woolfolk and Sanders (1987). The programme described covers relief at 2200 locations with valves ranging in size from $\frac{1}{4}$ in. to 12 in.

and made by 25 different companies. The SRVs are tested, disassembled, cleaned, examined, repaired, lubricated, reassembled, retested and sealed.

The original test equipment utilized a low air volume. The testing of SRVs on this was not satisfactory and it was replaced by a system of larger volume, which proved more suitable. The authors comment that it is sometimes claimed that where an SRV has a bursting disc installed below it, it can be tested *in situ*, but that since the volume between the disc and the valve is small, this is equivalent to the use of a low air volume test system.

In SRV testing, the valve seat usually receives attention to ensure that the valve is leak-tight. Woolfolk and Sanders also place emphasis on the guide area. This should be cleaned, polished and lubricated.

Woolfolk and Sanders give details of the test intervals which they generally use, which are as follows. A 12 month interval is used for boilers (local legal requirement), process vessels with heat sources, vessels containing corrosive chemicals, and positive displacement pumps or compressors; a 24 month interval is used for process steam headers and storage; vessels with no heat sources; and a 36 month interval is used for instrument air manifolds within dehumidified control rooms and lubricating relief valves on enclosed systems.

Methods have been developed for the *in situ* testing of pressure relief valves, as described by J.K. Rogers (1988). The principle is to overcome the closing force of the valve spring by the application of an external hydraulic force. Then from knowledge of the valve seat area and line pressure at the valve the set pressure of the valve may be determined. The test can also determine whether the valve has been fully stroked.

A critique of *in situ* testing is given by Woolfolk and Sanders, who express the view that it has limitations where there are aggressive fluids and that it could fail to detect corrosion, partly bent or galled stems, partially plugged nozzles and certain misadjustments.

Some case histories of relief valve maintenance are described by Anon (1977 LPB 14, p. 2).

21.14.3 Storage tanks

The maintenance of atmospheric storage tanks presents a quite different set of problems. Accounts are given by Huston (1983) and Shtayieh (1983a,b).

Maintenance of storage tanks often involves entry into the tank. In this case a large part of the maintenance activity is the purging and cleaning required before entry can be gained. This aspect is described in Section 21.12 and is not therefore repeated here.

As for pressure vessels, so with storage tanks, the ancillary features should be maintained in good condition. In particular, the tank vent system should be maintained by a system similar to that applied to relief valves on pressure vessels.

Most descriptions of storage tank maintenance are concerned with leaks. The case described by Huston involved a storage tank with a leaking floor, a not uncommon occurrence. The identification of leaks, which may be no more than 5 mm diameter, is usually difficult due to the poor lighting in the tank and to the state of the tank floor. The author describes a method of improving the detection of the leaks by forcing water under the tank and filling the underside of the floor with water, so that water comes up through the leaks.

An account of leak detection and repair in a refrigerated propane tank is given by Shtayieh (1983b). The tank was of double wall construction with insulation between the inner and outer walls. Monitoring of the gas space between the two walls showed the presence of hydrocarbons at a concentration of 15–20%, indicating the existence of leaks. A thermographic survey was carried out on the outside wall which showed two cold spots at a temperature 1.5°C lower than the rest of the wall. The tank was entered and eventually leaks were found. The main leak was on a manhole, where there was a faulty gasket and a badly machined blind flange gasket face and cover. There were two lesser leaks at the two 2 in. diameter nozzles of the guidewires of the level indicator, due again to damaged flanges. No leaks were found at the points suggested by the thermography. This example demonstrates the trouble caused by deficiencies in common installation activities, in this case the making up of flanges.

The author's account gives a good illustration of the entry, isolation, emptying, purging and entry procedures for such a storage.

21.14.4 Ammonia storage spheres

The occurrence of stress corrosion cracking in ammonia storage spheres has created a considerable problem in the maintenance of such storages. Accounts are given by R.S. Brown (1982) and Guth and Clark (1985). They illustrate both the procedures for isolation, emptying, purging and entry, and for bringing back on stream for such storages and the procedures for inspection and repair. This work is discussed further in Chapter 22.

21.14.5 Heat exchangers

Heat exchangers are pressure vessels, but in addition their maintenance is affected by certain characteristic features of their own. Accounts are given by Yokell (1983) and Fijas (1989).

Where a heat exchanger is delivered to a construction site and is left in the open for some time before it is installed, it may well suffer deterioration even before it begins operation. In order to avoid this, it should be stored carefully before installation and its surfaces cleaned periodically. The necessary measures are described by Fijas.

Heat exchanger tubes are liable to leak or even rupture and these faults may be induced by maintenance activities. One such activity is tube bundle withdrawal. There should be procedures for bundle withdrawal. The bundle should be supported on the tubesheets, baffles or blocks contoured to the bundle, but not on the tubes themselves.

It is usually necessary to clean the tubes to remove scale. If cleaning is deferred too long, maldistribution may occur in some tubes and the resultant differential thermal expansion of these tubes can cause damage and leaks.

Methods of cleaning heat exchangers are described by Fijas. Soft deposits may often be removed from the shell or tube sides of a heat exchanger by washing with hot oil and soft salt deposits by washing with hot fresh water. More stubborn deposits may be removed by chemical cleaning. He recommends against cleaning tubes by blowing steam through them, since it is liable to cause overheating and thermal expansion and thus

induce tube leaks. Nor should tubes be hammered with a metallic tool. If they must be scraped, the tool should not be sharp enough to cut them.

Heat exchanger tubes are subject to vibration, which is liable to cause leaks. One cause of tube vibration is operation at too high a fluid velocity. Another is vibrations transmitted from a pump or compressor. A pulsation damper may be used to reduce vibrations from such a source.

When starting up and shutting down a steam heated exchanger, condensate should be drained out as a precaution against water hammer. If shut-down is at all prolonged, it may be necessary to drain the fluids from the exchanger to prevent freezing or corrosion.

21.14.6 Equipment supports

Equipment supports provide another illustration of the interaction between design, inspection and repair. An account of the maintenance of such supports is given by B.N. Pritchard (1983). The types of support which he considers are concrete supports and steel supports fireproofed by encasing them in concrete. Causes of deterioration include corrosion, overstressing, frost damage and also fire or explosion.

Concrete protects buried steel against corrosion partly by constituting a physical barrier to oxygen and moisture and partly by passivation of the steel by water made alkaline by the concrete. This latter effect decreases as the alkalinity falls off.

If the steel under the concrete does corrode, corrosion products are formed which have eight times the volume of the steel which they replace. This creates stresses which result in cracking and spalling of the concrete.

The author reviews the effects on the corrosion of steel encased in concrete of chlorides, sulphates and acids. In rare cases it may be promoted by a cement aggregate reaction.

Corrosion of steel encased in concrete may be reduced by: the use of dense concrete; good steel—concrete bonding; shaping the concrete so as to exclude rainwater, or the use of rainwater flashings; and the application of a suitable coating to the outside of the concrete. The author states that for fireproofing cast *in situ* concrete appears superior to gunnite, though the reason is unclear.

Paint applied to the steel provides a degree of protection not only for bare steel but also for steel encased in concrete or provided with lightweight fireproofing.

Corrosion occurring inside the concrete casing may be detected by visual examination, and also by tapping. In general, hairline cracks are tolerable but stained cracks may indicate a more serious situation. For certain cases the use of more sophisticated inspection may be justified. Early detection is highly desirable. Suitable timings for inspection are at 1 year after commissioning or after a material change of duty or environment, and at 4 yearly intervals thereafter. Formal records should be kept of the supports and their inspection.

Factors which govern the repair of supports are the features which have caused the deterioration, the further deterioration expected, the effects of the damage on the structure, the importance of the structure, the operating history of the plant and the cost of repairs. The repairs should incorporate measures to remove the causes of the deterioration. Repair techniques include the sealing of cracks, cutting back to sound concrete and cutting back to the steel. Temporary supports may be necessary whilst repairs are being effected.

21.14.7 Foundations and bunds

Foundations and bunds also may require repair. Accounts of the repair of foundations are given by Renfro (1978, 1979). Containments are discussed by Hazen (1991).

21.15 Equipment Removal

The removal of equipment from the plant to the workshop can create a hazard if flammable or toxic material may be trapped inside it. It is necessary to have some procedure to deal with this problem.

21.15.1 Unused equipment

Equipment which is installed but is no longer required should normally be removed. This applies to all kinds of equipment whether it be vessels, pumps, pipes, instruments, fuses, etc. Unused and often disconnected equipment is a fertile source of accidents.

21.15.2 Equipment sent off site

Where equipment is sent away from the plant, whether for repair or because it is no longer required, the state of the equipment should be reviewed, any hazard identified and appropriate measures taken. In particular, there is the potential hazard that equipment may still contain residues of flammable or toxic material.

21.16 Deteriorated Equipment

The equipment on the plant starts to deteriorate from the first day of operation, and sometimes earlier if it has been neglected prior to installation. As the plant ages, it becomes necessary to take a view about the continued operation of some equipment.

21.16.1 Remanent life assessment

Some equipment is designed to have a limited life. The prime example here is equipment with a limited creep life. Creep is described in Chapter 12 and the shortening of creep life by abuse during operation is discussed in Chapter 20. Where there is reason to think that the latter has occurred, it may be necessary to attempt an assessment of the remaining life.

Another major form of deterioration is corrosion and, insofar as a particular corrosion allowance is made, in this case also the design implies a limit to the life of the equipment. The possibility of periods of corrosion at rates much higher than average means that here too there is a need for life assessment.

The assessment of the remaining useful life of equipment, or the remanent life assessment (RLA), is an established activity. It is described by Baker-Counsell (1987b) and Grosshandler (1987a). If the equipment is nearing the end of its life, remanent life assessment provides the necessary wanting, whilst if it still has an appreciable fraction of its life left, the RLA provides assurance that it can continue in operation.

Much work in remanent life assessment is concerned with creep effects. Some techniques used are

metallography, strain measurement, accelerated creep testing and stress analysis. The results of RLA may be expressed as a cumulative probability of failure, which allows the company to make its own judgement on how much longer to continue to operate the equipment.

A specific example of the application of remanent life assessment to corrosion of a pressure vessel and its nozzle is described by Grosshandler (1987a). Further accounts of obsolescence include those of Munro (1963) and Baas and Warner (1992), who describe the assessment of the remaining useful life of an ethylene plant.

21.16.2 Used equipment

The situation can arise where it is necessary to consider either the purchase or the sale of used equipment. Some of the considerations which arise have been described by J.P. Epstein (1967, 1978) and C. Butcher (1992d).

For purchase, three approaches may be taken: purchase 'as is', on approval, and rebuilt and guaranteed. Most equipment is bought 'as is'.

When purchasing equipment, checks should be made on: the dimensions of equipment; the pressure integrity of pressure vessels; the wear sustained by moving parts of machinery; any ancillary equipment; and conformance to any regulatory requirements. Useful information can often be obtained by inspecting the equipment whilst it is still on site and in use. Equipment allowed to stand idle even for a short time acquires grime, but a grimy appearance does not necessarily betoken a poor general state.

Specialist companies exist which deal with used equipment and it may be beneficial to use their expertise.

21.16.3 Fire damaged equipment

In the aftermath of a large fire, there may be equipment which has been in the fire. The question then arises as to the continued safe use of the equipment. In all such cases a check should be made. Pressure system integrity is of particular importance and should be investigated by experts.

A case history of the assessment of fire damage of a vessel is described by Dooner (1986). The vessel was to be used in a low temperature application down to −196°C. It had been in a fire which lasted some 2 hours and subject to an estimated temperature in the range 400–600°C. A metallurgical investigation showed that no significant deterioration had occurred and the vessel was put into service.

21.17 Some Maintenance Problems

21.17.1 Materials identification

Misidentification of materials is a significant problem. Mention has already been made in Chapter 19 of errors during the construction and commissioning stages, particularly in the materials used in pipework. Materials errors also occur in maintenance work. Situations in which they are particularly likely are those where materials look alike, e.g. low alloy steel and mild steel, or stainless steel and aluminium painted steel. It is necessary, therefore, to exercise careful control of materials. Methods of reducing errors include marking, segregation and instrument spot checks.

21.17.2 Component identification

Another problem is mistakes in identifying components or equipments. Confusion can arise, for example, over pressure relief valve components, with the result that a relief valve may be put back on the plant with too high a setting. This type of error can readily occur with similar components made by the same manufacturer. Similarly, it is easy for slip plates to become mixed up so that a slip plate suitable only for a low pressure duty is used on a high pressure application.

A particular type of component identification error is fitting an equipment with a component that alters its performance. Thus the capacity of a control valve may be increased by putting in the wrong trim, or the delivery pressure of a pump may be increased by fitting the wrong impeller.

21.17.3 External corrosion

External corrosion beneath lagging is a considerable problem on process plant. It has already been described in Chapter 12. It is important that the maintenance system should check on external corrosion.

Such corrosion occurs particularly on steel equipment in the temperature range 0–125°C. Below 0°C the surface is protected by ice, while over 125°C water evaporates. Use of types of mineral wool insulation that are acidic can exacerbate the problem.

There are various forms of corrosion which can occur due to agents other than water. Chloride attack occurs from chlorides which are leached out of some insulation materials. It can also arise from thermal decomposition of polyvinyl chloride (PVC) labels on very hot pipe surfaces. Nitrate attack arises from the use of nitrite treated water on plant surfaces.

Supports for storage tanks and vessels are a common site of external corrosion.

21.17.4 Pumps and other equipments

Pumps are the source of a large proportion of leaks and fires on process plant. A common fault is seal failure with resultant leakage. The leakage often ignites and causes a pump fire. Another frequent fault is a bearing failure, which can induce a seal failure. After a pump fire it is not always easy to tell whether the seal or bearing has failed first.

Reduction of pump failures is partly a matter of design and selection, but maintenance aspects are also important. Many faults can be forestalled by a careful overall check when a pump is taken off for other maintenance work.

In addition, it is not uncommon for faults to be introduced in the course of maintenance work. A simple example is misalignment of the impeller shaft when the pump is reassembled. Faults of this kind point to the need for proper systems of work for maintenance and for adequate training. Similar problems arise with other types of equipment.

21.17.5 Small bore connections

Small bore connections are another source of leaks and fires. Such connections are often abused. Heavy pressure gauges or valves may be fitted to them without adequate support. They are frequently overtightened, sometimes with a pipe wrench. People may stand on them to reach isolation valves.

21.18 Major Shut-downs

Two particular kinds of shut-down merit specific mention. These are major scheduled shut-downs and mothballed shut-downs.

21.18.1 Scheduled shut-downs

Most plants require a periodic major scheduled shut-down, or turnaround, in order to carry out maintenance and other jobs which cannot be done whilst the plant is operating. Accounts of turnarounds are given by Vargas (1979), Tropp (1986) and Feuless and Madhaven (1988).

The turnaround arrangements described are broadly as follows. The responsibility for the turnaround is assigned to a turnaround manager. The turnaround passes through four stages: (1) formulation, (2) planning, (3) implementation and (4) start-up.

In the formulation stage the turnaround manager solicits job requests from the interested parties. Each job is defined, given a priority rating and assigned to a person who is responsible for it. Three levels of priority may be used: (1) the job can be done only during turnaround and has high priority; (2) the job can only be done during turnaround, but is not critical; and (3) the job can, if necessary, be done outside turnaround. The responsibilities for the total set of jobs are spread widely, but for each job there is only one person responsible. A deadline is set a few weeks before the turnaround start date, and thereafter only priority jobs are accepted. A master job list is drawn up and a critical path network developed for each job. The parts and special tools required for each job are identified and the process is begun of obtaining them and transferring them to the turnaround lockup.

Tropp (1986) states that the two faults to which turnarounds are most subject are unsuitable assignment of responsibilities and inadequate exchange of information. The normal roles which people play are often not appropriate to a turnaround. Failure to recognize this is a main cause of communication failures.

He describes a system of categorization of jobs by logical, chronological and priority groups. With regard to the first two, the logical group covers categories such as time, information, safety, manpower, materials, tools, etc., and the chronological group covers those of preparation, implementation and review. He gives detailed responsibility charts for the preparation and implementation stages. Entries in the chart are R, I, C and N for responsible, implement consult and notify, respectively.

In the planning stage the overall critical path network is developed together with a bar chart showing the start and end time of each job and the personnel required. A manpower requirements list is drawn up. Computer aids are available to assist in such planning. The plan needs to be flexible and able to accommodate unexpected jobs. Work continues to ensure that the parts and tools required are moved to the lockup and a parts review is carried out to ensure that nothing is missing.

Throughout the formulation and planning stages there should be meetings to ensure that all interested personnel understand their role and make an appropriate contribution to the plan.

The job times should be the subject of detailed review by estimators. Use may be made of a library of job time estimates. In estimating job times allowance should be made for the fact that the time spent on turnaround jobs tends to be rather longer than that spent on equivalent routine jobs, and the fact that time is required to fetch materials, to purge and clean, and to await supporting functions such as safety or inspection.

Some of the worksheets developed are illustrated by Vargas (1979) and Feuless and Madhaven (1988). The former also gives a detailed account of the critical path scheduling.

The management of the implementation stage needs to be sufficiently flexible to accommodate the facts that some jobs may reveal problems, that some may take longer than planned, or require parts other than those expected, or that some completely new jobs may need to be done. It is not uncommon for 25% of the jobs done in a turnaround to be identified only at this stage. A meeting of those concerned is normally held at the start of the day to report progress and to modify plans as necessary.

There needs to be a procedure for dealing with those cases where the parts or materials specified are not available and the use of some alternative is proposed. For example, pipework in some special steel may be on too long a delivery and there may be an intention to use a substitute material, or the type of pressure transducer specified may be unavailable but another type may be to hand which is apparently equivalent.

The purpose of the turnaround is to get the work completed and the plant started up again. The emphasis, therefore, should be on the start-up, rather than simply completion of the turnaround.

When the start-up is over, the personnel involved should be debriefed and a report written whilst matters are still fresh in the mind. In particular, note should be made of times actually taken and the resources used for various jobs and activities, of problems encountered, equipment required, techniques developed or lessons learned, and of jobs which will need to be done in the next turnaround.

As soon as the turnaround is over, preparation for the next one should begin. Many of the jobs in the latter will be based on the inspections just made.

21.18.2 Mothballed shut-downs

During an economic recession, the decision may be made to take a plant out of commission and to 'mothball' it, with a view to recommissioning it when times are better. Accounts of mothballing, and demothballing, are given by Twigg (1985), R.G. Miller and King (1987) and Savage, Portnoy and Parkinson (1988).

Mothballing is applied to a variety of installations and equipment, including oil field production systems, refineries, chemical plants, drilling rigs, oil tankers, and special equipment. It is much used for military equipment, including vehicles, ships and aircraft.

The mothballing of plant is not an exercise to be undertaken lightly and the alternatives of selling or scrapping it should be carefully considered. The circumstances which make decommissioning necessary are attended by a number of problems. Personnel may well be somewhat demoralized. There is uncertainty as to how long the plant will be out of action. There is likely to be pressure to do a cheap job. The staff concerned will generally lack experience of laying up a full

installation. The compilation of a complete set of documentation for the plant is an unattractive chore.

There are a number of factors that affect the way in which the mothballing is done. The length of the shut-down is relevant, since the measures required to preserve the plant for a few months differ from those required to preserve it for 10 years, but is often unknown. The location affects factors such as the climatic conditions and vandalism. A hot, humid site promotes corrosion. A rundown urban area is more prone to theft and damage by outsiders. Some plant fluids such as seawater and sour gas are more corrosive and some materials of construction such as stainless steel have particular vulnerabilities.

It may not be appropriate to mothball every item. Some items of equipment and much instrumentation are particularly prone to obsolescence. For other items, such as small bore pipework and valves, it may be more economic to let them go and replace them when the plant is recommissioned.

There are a number of methods used to guard the plant against corrosion and other deterioration whilst it is mothballed. Items of equipment may be removed from the plant and stored after suitable treatment in a warehouse. Measures may be taken to ensure that the fluids in the plant are benign. Examples are replacing seawater by fresh water, purging with nitrogen and adding an inhibitor to condition vapours. The equipment can be isolated from its environment by the use of various forms of barrier such as: paint; greases and waxes, known as slushing compounds; boxes or bags; or cocoons. Other anti-corrosion measures may be taken, such as the use of cathodic protection. Some parts of the plant may be kept in continued operation and some items may be periodically stroked or rotated, as the case may be. Methods particularly favoured by the military are the use of greases and waxes, and of cocooning.

Corrosion is liable to be much higher during a prolonged shut-down than in normal operation. R.G. Miller and King (1987) contrast a storage tank corrosion loss of 3 mpy (thousandths of an inch per year) in normal operation with one of 100 mpy in the shut-down condition, with an associated change from general to pitting corrosion. Corrosion may be worst in summer as warm air is driven out of equipment during the day and cold air with high humidity is drawn back in at night.

Cooling water systems can be troublesome unless suitable precautions are taken. Failure to protect adequately can result in rust and scale blocking of the tubes of heat exchangers all over the plant for months, or even years, after restart.

One form of internal corrosion which often occurs is microbiological corrosion. Precautions against this involve the use of good quality water and of organic biocides. Chlorination of the water tends to be ineffective.

If equipment becomes severely corroded, the penalty can be high. A case is quoted by Miller and King where breaking the line at a spool piece with corroded bolts took a team of five men using heavy equipment 5 days.

Two widely used methods of reducing corrosion are the use of dry inert atmospheres in vessels and the coating of surfaces with oil. Corrosion is reduced by the exclusion of oxygen, and filling vessels with nitrogen is an effective anti-corrosion measure. The gas should be dry, with a dewpoint at least 5°C below that of the lowest expected ambient temperature.

Oils or oil-based products can be used to reduce corrosion. Refinery equipment is frequently protected by filling it with oil and then running the oil out again. The thin film of oil gives protection until it eventually drains down. Alternatively, surfaces may be coated in oil or grease. Small items may be dipped in oil. Vapour phase inhibitors may be used for areas which are not readily wetted by oils.

The type of protection provided against corrosion may be matched to the intended period of shut-down, if this is known. Twigg suggests that for short period shut-downs it may often be sufficient to flush and drain, whilst for longer ones greasing or painting may be necessary. Similarly, Miller and King suggest that for some equipment washing down and coating with diesel oil may suffice for a shut-down of 18 months, whilst shot blasting and painting may be preferable for one lasting 5 years.

External corrosion is liable to occur under insulation and on equipment supports. Features which promote such corrosion are damage to the insulation and chlorides from the insulation. One policy sometimes adopted to combat external corrosion during mothballing is to remove the insulation completely. Alternatively, if the insulation is not removed, any damage to it should be made good and it should be sealed.

Cocooning involves the use of strippable plastic coatings and gives an enclosure not dissimilar to vacuum packing. It can be very effective provided that moisture is excluded but moisture can pass through due to the breathing of the membranes and corrosion can occur unless the dewpoint of the air inside is kept low. The coatings have a tendency to come off in high winds.

Valves left unused for long periods are liable to seize up due to the hardening of lubricants. One solution is to remove them to store. Another is to leave them in but maintain and operate them occasionally.

Some parts of the plant may best be preserved by operating them periodically. Savage, Portnoy and Parkinson (1988) describe the preservation of a cooling system by running a high chromate solution through the system once every 2 weeks throughout the mothball period.

Rotating equipment should be turned at intervals to avoid 'brinelling'. Frequencies recommended are typically in the range 1–6 months, depending on the type of bearings.

Cannibalization of the plant should not be permitted. Where there is a protective envelope, breaking in can negate it and lead to severe corrosion. The loss of parts is liable to be disproportionately disruptive when the time comes to recommission the plant. Moreover, when equipment is removed in this way, damage is frequently done to other items.

The mothballing of plant does not remove the need to inspect and maintain, or even to operate parts of it. Inspection is still required, but the techniques involved are somewhat different. There is also a need for some degree of maintenance.

A full set of documentation on the plant, and on its operating and maintenance procedures, needs to be compiled. Such documentation is necessary for any plant, but it is crucial for one which is to be recommissioned

at some date in the future by personnel who are likely to be unfamiliar with it. The documentation should include full details of the mothballing itself, of any items removed from the plant and the state of the remaining plant.

The methods of protection used in mothballing may also be applicable where equipment arrives on site but cannot be installed immediately. Heat exchangers in particular are prone to deteriorate rapidly if left unprotected prior to installation.

The problems which arise when demand turns up and demothballing can be considered are discussed by Savage, Portnoy and Parkinson. Again there are often alternatives such as debottlenecking and revamping existing plants or building new plant, and, in view of the problems likely to be encountered in recommissioning, these should be given full consideration. If recommissioning is decided on, it may well be combined with modifications to the plant to achieve better product quality, higher output or improved efficiency. A prerequisite for recommissioning is the retrieval of a fulll set of documentation on the plant.

Some items or systems are likely to have suffered considerable deterioration. Some equipment, such as valves, may well need to be reconditioned and some, such as small bore pipework, may need to be replaced. Other equipment may need replacement due to obsolescence, which is particularly rapid in some instances, such as the instrument systems, including computers.

It will be apparent from the account just given that in addition to all the usual measures necessary for a commissioning, a recommissioning after mothballing needs to be preceded by an extremely thorough inspection of the plant and review of the documentation if hazards are to be minimized.

21.19 Maintenance System

21.19.1 Maintenance information system

Information on plant incidents, failures and repairs is needed both for maintenance and SLP purposes. It should be a specific objective of the maintenance system to generate such information.

The principal data required are those for failure, repair and availability. The data are more valuable if they are of good quality. Failure data should preferably give for each equipment the time to failure in each failure mode rather than overall failure rates. Availability data should give throughput density rather than a single downtime figure. There are also other data which are needed. These include data on leaks and fires and on human errors.

Data on failure and related aspects are essential to the loss prevention approach. The plant engineer, therefore, has a crucial role to play here. He should make it his business to have an information system which generates these data. Such data are equally useful, of course, to the plant engineer himself. He normally monitors failures and failure modes at least in a semi-quantitative way, but if higher quality data are available he can analyse them to obtain additional information. Thus an early failure (Weibull parameter. $\beta < 1$) may point to the need for better supervision or training of maintenance workers or for the work to be done under less dirty conditions, while wearout failure ($\beta > 1$) may indicate the possibility of preventive replacement.

21.19.2 Maintenance information feedback

The requirement for failure data is one aspect of the more general need for feedback of information from the maintenance to the design function. This is the theme of terotechnology, which is discussed in relation to maintenance by Husband (1976). Again the plant engineer can play a key role in ensuring effective feedback of information and so reducing unreliable and hazardous features, and he should make this a definite objective.

21.19.3 Maintenance policies and effectiveness

The maintenance policies which are followed in a process plant can have a marked influence on its reliability, and availability, and hence its safety and economics. There is, however, no universally applicable policy. The policy appropriate in a given case depends on the failure pattern and the overall situation. Traditional policies have been based on breakdown maintenance and/or scheduled maintenance, and also opportunity maintenance, which are supplemented increasingly by on-condition maintenance and reliability-centred maintenance.

The effectiveness of the maintenance should be monitored using measures suitable for the policy adopted. Maintenance policies and effectiveness have been discussed in more detail in Chapter 7.

21.19.4 Maintenance of protective devices

Maintenance of the protective devices on the plant is particularly important and should be covered by a formal system with full documentation.

Some of the principal protective devices are:

(1) pressure relief valves;
(2) bursting discs;
(3) tank vents and filters;
(4) other pressure relief devices;
(5) non-return valves;
(6) mechanical trips and governors;
(7) instrument trips;
(8) other instrumentation;
(9) alarm systems;
(10) fire and gas detection systems;
(11) sprinkler systems;
(12) fire water systems.

This list includes not only the more obvious protective devices, such as pressure relief valves, but also some other critical items which are not always thought of as protective devices, such as tank vents.

The maintenance of instrument trip systems is very important. The design of such systems is based on the assumption of proof testing at fixed intervals and is invalidated if this is not done correctly.

It is also important that the other instrumentation be maintained to a high standard. If the general instrument system is allowed to degrade with numerous incorrect measurements, false alarms and control loops on manual, the probability of control errors is greatly increased.

Fire protection equipment should be well maintained so that it is available when required. There have been many instances where equipment has failed to operate, often with serious consequences. Maintenance of such equipment is dealt with in NFPA 13A: 1987 *Inspection, Testing and Maintenance of Sprinkler Systems* and NFPA

14A: 1989 *Inspection, Testing and Maintenance of Standpipe and Hose Systems.*

21.20 Spares Inventory

The control of the spares inventory, or stock control, is of particular importance on process plants, where the cost of downtime is generally very high. Accounts are given by Alford (1965), Corder (1976), Husband (1976), A. Kelly and Harris (1978), Vargas (1980b) and D.J. Smith (1985a). Generally, the proportion of management effort devoted to spares inventory control is small relative to that given to control of the workforce.

21.20.1 Spares holdings

Policy on the spare parts to be held in stock has to be a compromise between holding a large number of parts in an attempt to provide for virtually every contingency and holding only a small number in order to keep holding costs down. Some studies of maintenance systems have highlighted spares, or lack of them, as the main problem faced by the maintenance function.

Standard methods of stock control are the maximum–minimum level and the economical order quantity methods. The former sets minimum and maximum stock levels together with a reorder level. The economical order quantity for an item is given by the relation

$$Q = (2RP/H)^{1/2} \qquad [21.20.1]$$

where H is the annual cost of holding the item, P is the cost of procuring it, Q is the optimal order quantity and R is the annual requirement. This formula takes no account of the criticality of the item, the lead time for its delivery or of the relationship between the item and other items.

The methods of reliability engineering may in certain cases be used to determine the spares holdings. Some reliability models which may be used for this purpose are described by D.J. Smith (1985a). For an equipment which has n identical parts and a spares holding of r parts and for which the failure rate of these parts is known, the Poisson distribution may be used to determine the probability that over a specified period a situation will arise where the spares have run out. This model assumes that the equipment is a series system with respect to the n parts; it does not take account of any redundancy in the equipment involving some of the n parts or of the time to replace a part. These and other features may, however, be taken into account by the use of Markov models.

It is concluded by Husband that the soundest approach to the use of models may often be to base the holding on Pareto analysis of the main relevant features such as usage, criticality, lead time and cost.

Guidance on spares holdings may be available from the equipment manufacturer in the form of a recommended list of parts to maintain the equipment for a specified period. Such a list will generally be based on the manufacturer's experience and judgement. It may also utilize information on the number of parts which have been supplied to users on request. This information is hard data, but is liable to be incomplete, because many parts are either ordered from other suppliers or fabricated by the user company itself. It may well be, therefore, that better information even on the frequency of demand for particular parts is generated by the maintenance function itself. Certainly, this is in a better position to assess the criticality of items and the lead times.

The level of spares will be affected by the degree of standardization. Indeed, it is a principal aim of standardization to reduce spares holdings.

Another feature affecting spares holdings is the least replaceable assembly. This is the module or part at which during maintenance the process of fault diagnosis terminates and a replacement is effected.

Some of the factors relevant to the setting of spares holdings which are unique to a single equipment are the tolerable unavailability of the equipment, the failure frequency of the parts, the lead time and the costs of the parts.

Where spares are common to a number of equipments, the situation may become either more complex or simpler. If the number of other equipments is small and the failure frequency of the parts is low, it may be necessary to consider the set of equipments as a whole and the interaction between them. But if the frequency of demand for the parts becomes high, the simpler treatments such as the Poisson model may well become applicable.

Many accounts of spare holdings treat the demand for spares as a random process. In fact, where preventive maintenance (PM) is practised, the demand for spares for PM work is more predictable, and this fact may be exploited. Moreover, PM will also identify cases where parts will be needed in the near future.

Management should assess the need to hold slow-moving but critical items, and unjustified pressure to reduce the holding of such an item should be resisted. It may be possible to quantify the probability of requiring such an item and of not having it in stock and the consequences and costs of such a situation. But in any event it may be regarded as an insurance.

The spares holdings will be strongly affected by the extent to which a 'just-in-time' policy is practised. Whilst, in principle, many of the factors just described still apply, the actual values of the optimum spares holdings may be appreciably different.

21.20.2 Stores organization

Features of the spares organization are the stores layout, the stores documentation, the coding system, policies on aspects such as used parts and cannibalization of parts, and access to the store. An explicit policy should be formulated for the stores and their organization.

Plant spares may be grouped either by plant equipment or by common items, the latter being common to a number of plant equipments, e.g. bearings and seals. The system may well be a hybrid. There are three main types of item held in a store: plant spares, consumables and tools.

The stores documentation should be designed to implement the stores policy. An account of typical stores records is given by Corder (1976). Since the use of computer systems is virtually universal in maintenance, the documentation must be compatible.

The system for coding of items is liable to become extremely cumbersome unless it is well designed. Corder

gives the example of a bearing made by three bearing manufacturers and installed in the machines of six machine manufacturers, which then may well have 18 different code numbers. He discusses the method of classification and coding designed to overcome this.

It is necessary to establish a policy with respect to used parts. Parts may be reconditioned and returned to the store, but the mixing of used and deteriorated parts with new or as-new parts is not good practice.

A policy is also required on cannibalization. This can be extremely disruptive, which is an argument for prohibiting it. On the other hand, situations are likely to arise where a rigid ban could not only be very costly but could bring the policy into disrepute. It may be judged preferable to have a policy to control it.

Access to the store should be controlled, but in some cases it is policy to provide an open store with free access for minor items, where the cost of wastage is less than that of the control paperwork.

Materials for a major project should be treated separately from those for normal maintenance. Failure to do this can cause considerable disruption to the maintenance spares inventory. In this context a turnaround may count as a major project requiring its own dedicated store, as already described.

21.21 Computer Aids

The use of some form of computer system is virtually universal for maintenance systems on process plants. Accounts are given by Trotter (1979), Redding (1980), McChrystal (1982), Collington (1989) and Project Software and Development Inc. (PSDI) (1991) and M. Taylor (1991).

Some functions which a computer-based maintenance information system may perform include (1) work orders, (2) planning and scheduling, (3) failure analysis, (4) costing and (5) budgeting.

Many computer-based systems have started as accounting systems dealing with the costs of maintenance work. Such systems may or may not adapt readily to a wider variety of functions. The constraints which may be posed by an existing system are not considered further here. It is taken as read that the maintenance system will link closely with the accounting system.

Another system with which the maintenance system should link, and with which it may well be integrated, is the system for equipment inspection and inspection records.

The design of a computer-based system should start by trying to ensure that the source of data fed to it is of high quality. This is both important and difficult. The people who have the much of the information required are the maintenance craftsmen who do the actual work. The problem has traditionally been that these craftsmen are reluctant to spend time on paperwork.

With a manual system it is difficult to give maintenance personnel much incentive to furnish high quality information. A computer-based system, however, does provide the means of offering such an incentive by creating a system where they have access to information which is useful to them.

The basic building element of a computer-based system, as of a manual one, is the work order. Work orders for regular jobs can be held and orders for new jobs entered. The work order for a particular job will generally contain a wide range of information such as on labour, spares, timing and costs, which provide the much of the basic data for the other features of the system.

Closely linked with the work order is the job ticket issued for performance of the work. The system facilitates the generation of job tickets which give a complete description of the work to be done. This makes it easier to ensure that nothing is missed and that even small faults are corrected before they escalate.

A computer-based system is a natural tool for the planning and scheduling of the work orders. This includes orders both for breakdown maintenance and for preventive maintenance. Resources such as labour and equipment can be scheduled. Schedules can be formulated to accommodate backlogs and priorities.

Failure analysis is another widely utilized function, but the meanings attached to this term vary. It may involve an analysis of the causes, frequency and cost of repairs. Or it may extend to more sophisticated analyses such as Weibull analysis to determine the failure regime.

As already mentioned, costing was one of the first functions exploited. There is a variety of features which come under this heading. Elementary features include the costing of labour and parts. For routine jobs standard cost estimates may be held. More advanced costing features include the handing of depreciation and assisting decisions on repair vs replacement.

Budgetary control is a standard feature, which facilitates not only determination of the budget for some forthcoming period, but control of day-to-day expenditure.

It may be advantageous to order items in a hierarchy within the system so that an overview can be obtained not only of basic elements but also of aggregations which constitute complete equipments or plant functions.

There are a number of pitfalls in the implementation of a computer-based system. One is the input of the initial data. One strategy to ease this task is to identify critical features and enter them, and then to build up the rest as particular jobs arise.

Experience of computer-based systems indicates a number of beneficial effects. One is that effort is freed so that more attention can be devoted to planning and to preventive work. A simple example cited is a reduction in the ratio of breakdown to preventive maintenance jobs from 10:1 to 2.5:1. The reduction in the proportion of breakdown jobs means that the maintenance function gets more on top of its work and enters a virtuous circle. As preventive work becomes relatively more prevalent, the timing of such work becomes less critical, since the equipment is a better state of maintenance.

Another important benefit is in increase in the credibility of the maintenance function, because the data are to hand to support arguments by quoting chapter and verse. Improved relations with the operations function is another gain, signalled when production take the initiative in asking for equipment to be included in the PM schedule. More generally, an effective computer-based maintenance system becomes an important resource for many other functions, notably those of design and SLP.

The use of a computer-based system to handle the problem of a half-yearly PM whose schedule has slipped is outlined by Collington (1989). He describes in effect

the creation of a form of expert system to assist with the current and future decisions.

A description of a particular computer-based system for an LPG terminal has been given by the PSDI (1991).

21.22 Modifications to Plant

Some engineering work on plant goes beyond mere maintenance and constitutes modification. Such modification involves a change in the plant and/or process and can introduce a hazard. The outstanding example of this is the Flixborough disaster. The *Flixborout Report* (R.J. Parker, 1975, para. 209) states: 'The disaster was caused by the introduction into a well designed and constructed plant of a modification, which destroyed its integrity'.

It is essential, therefore, for there to be a system of identifying and controlling modifications. Modifications may be made to the plant or the process, or both. It is primarily plant modifications which are discussed here, but some consideration is given to the latter.

The control of plant extensions is dealt with in *Major Hazards. Memorandum of Guidance on Extensions to Existing Chemical Plant Introducing a Major Hazard* (BCISC, 1972/11). The hazards of plant modification and systems for their control are discussed by, Henderson and Kletz (1976) and by Heron (1976). Selected references on plant modification are given in Table 21.4.

21.22.1 Types of modification

Modifications may be classified according to the stage of the project at which they are made:

(1) design modifications;
(2) commissioning modifications;
(3) operating modifications.

They may be distinguished by the degree of permanence:

(1) temporary modifications;
(2) permanent modifications.

They may also be classed by the level at which expenditure decisions are made:

(1) non-sanction modifications;
(2) sanction modifications.

Table 21.4 *Selected references on plant modification*

IChemE (1966/43, 1985/125); FPA (1970/10, 11); K. Wood (1971); BCISC (1972/11); Booth (1976); Cannon (1976); Henderson and Kletz (1976); Heron (1976); Kletz (1976i, 1982i, 1984d, 1985g, 1991d); W.W. Russell (1976); Anon. (1980 LPB 34, p. 1); van den Berg *et al.* (1980); R.E. Sanders (1983, 1992, 1993b); Wang and Patel (1984); Baker-Counsell (1985e); Sha and Bohlinsky (1985); Speedie (1985); MacFarlane (1986); R. Atkinson (1987); Eishout and Kilstrom (1988); Kesler (1988); Ramsay (1990); Tian and Wang (1990); Anon. (1994 LPB 119, p. 17); Anon. (1994 LPB 120, p. 13); Turney (1994 LPB 120)

Modification chains: Kletz (1986f)

Plant retrofitting, updating: NRC (Appendix 28 *Retrofitting*); Kletz (1981e,h)

These different situations tend to have their own characteristic hazards. Some of these are illustrated by Case Histories B52–B56.

Modifications made during the design process really fall outside the present discussion, which is mainly concerned with the stages of commissioning and operation. It is sufficient here to re-emphasize the points already made concerning the need to ensure that at the design stage there is an adequate system of identifying and keeping track of any modifications made. The commissioning stage, and the immediately preceding pre-commissioning stage, is often a period when large numbers of modifications are made, frequently under intense pressure. Commissioning modifications tend to be aimed at making the plant work. In the operations stage the object is rather to keep the plant going. But again modifications may be done under considerable stress.

The scale of modifications and the level at which expenditure is sanctioned vary greatly. At one extreme there are minor modifications which require no special sanction. Until fairly recently the sole documentation on such modifications has been workshop job tickets or permits-to-work. At the other end of the scale are modifications requiring expenditure sanction by senior management. Such sanction requirements have traditionally been imposed to control costs rather than ensure safety, but they do at least usually result in a detailed consideration of the proposal by experienced personnel.

21.22.2 Pressure relief and blowdown hazards

A hazard which is liable to arise as a result of modifications and one which is particularly dangerous is the invalidation of arrangements for pressure relief and blowdown. Some illustrations of the way in which this can occur have been given by Henderson and Kletz (1976) and are shown in Figures 21.9–21.11. The situations are self-explanatory.

Another type of modification is the derating of a plant to a lower operating pressure. In this case, while the need to alter the pressure relief valve setting is usually appreciated, it is sometimes forgotten that it is necessary also to check the relief valve capacity, which is reduced by the derating. Similarly, an increase in plant throughput may require a change in pressure relief valve capacity.

The ease with which hazards associated with pressure relief can arise means that the check that the modification has not invalidated the pressure relief arrangements is particularly important.

21.22.3 Other hazards of modifications

Other hazards which can arise due to modifications are exemplified by the case histories given in Appendix 1. Some of the general features from these are considered here.

Modifications can invalidate not only pressure relief but also instrument systems. In particular, a situation may be created where an important measurement signal is degraded by the interposition of a restriction, filter, etc. This is illustrated by Case History B52.

A common modification is the temporary replacement or bypassing of a unit such as a reactor or heat exchanger with a length of pipe. This appears to be a

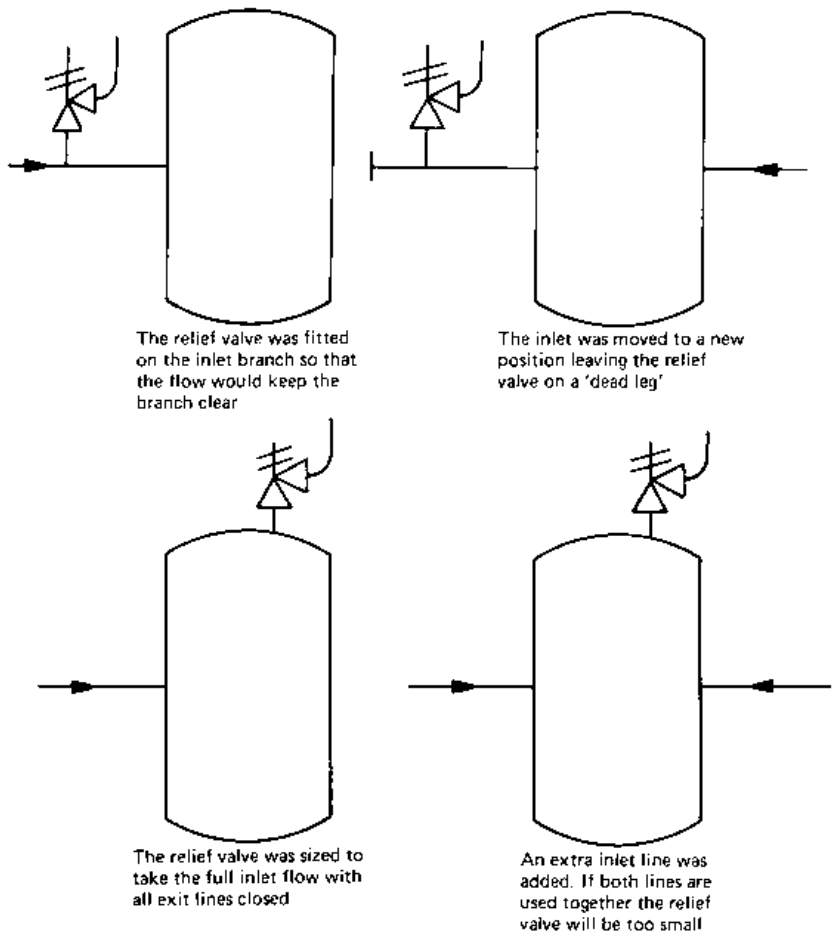


Figure 21.9 *Modifications invalidating pressure relief arrangements – 1 (Henderson and Kletz, 1976) (Courtesy of the Institution of Chemical Engineers)*

simple matter, but it is still necessary to design the pipe properly and to provide supports. The hazard is shown by the Flixborough disaster.

An alteration of a device which in some way limits flow or pressure can create a hazard. Examples include the removal of a restrictor orifice installed specifically to restrict flow, and the increase in the size of a valve trim or installation of a pump impeller capable of a greater head.

Modifications which appear quite minor can nevertheless introduce hazards. This is illustrated by Case History B56. Other hazards are listed in the form for the control of modifications shown in Figure 21.12.

21.22.4 Modifications to the process

The lesson commonly drawn from the Flixborough disaster is the importance of maintaining the integrity of the plant and of avoiding degradation due to a plant modification. The plant can also be put at risk, however, by the operation of the process outside the envelope of operating conditions for which the pressure system is designed. It is essential, therefore, to control such process modifications as well.

Moreover, even if the envelope of operating conditions remains the same, a change in operating practice may affect features such as inspection and proof test intervals, which tend to be based on historical plant experience.

21.23 Control of Modifications

The elements of a system for the control of plant modifications are (1) procedures, (2) assessment, (3) inspection, (4) documentation and (5) training.

There should be a formal procedure which requires all modifications to be authorized by competent persons and a standard method of making the safety assessment;

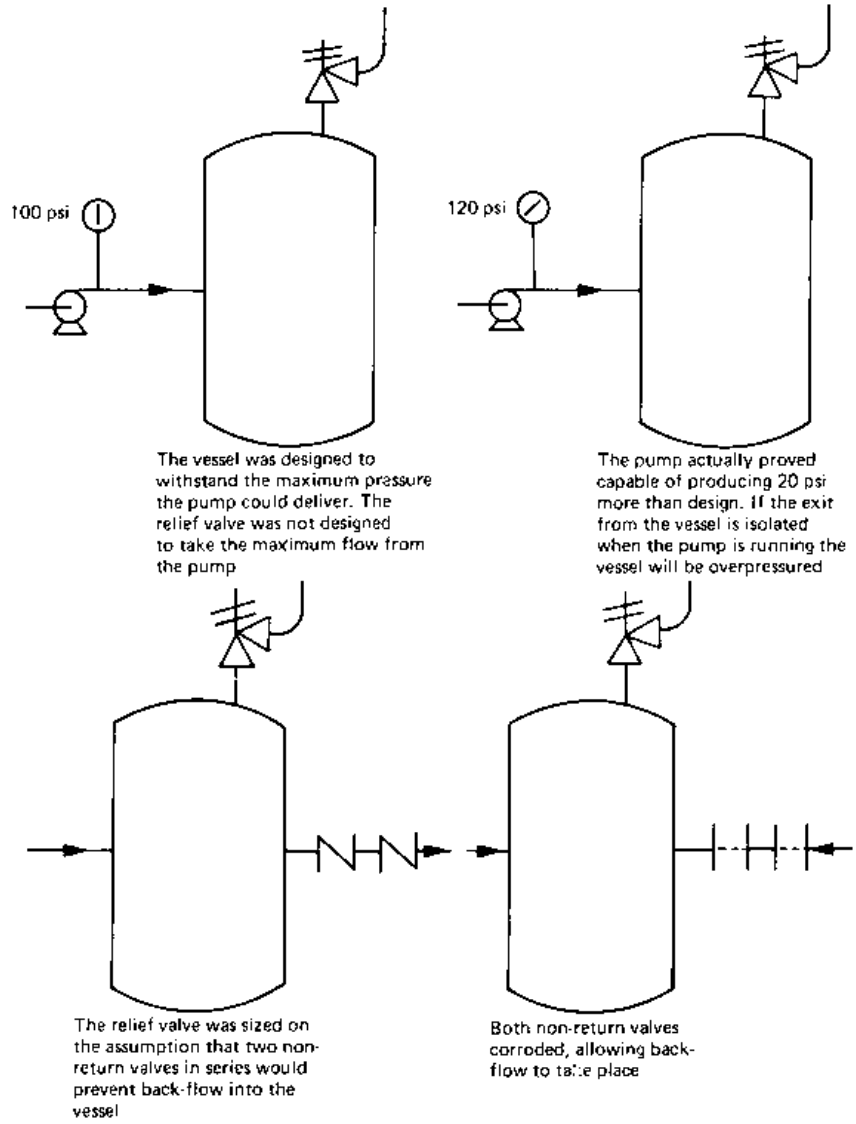


Figure 21.10 *Modifications invalidating pressure relief arrangements – 2 (Henderson and Kletz, 1976) (Courtesy of the Institution of Chemical Engineers)*

there should be a system of inspection of modifications by a competent person to make sure the work has been done as intended and is complete; there should be a system of documentation to record the change; and there should be adequate training so that all personnel concerned understand the system of control.

21.23.1 Authority for modifications

Systems for the control of modifications and the levels at which particular types of modification can be authorized vary somewhat, but the basic principles are quite clear. There should be a well defined and understood system of authorization.

The system described by Henderson and Kletz (1976) is that any modification to a plant or process must be authorized in writing by a competent manager and engineer. This applies to any modification, however cheap and temporary, as well as permanent modifications. The level of authorization is usually the lowest level of technical executive management, i.e. plant manager and plant engineer. If the modification involves instruments or electrical equipment, an instrument or electrical engineer should also approve the modification.

It is essential that these works personnel be capable of recognizing problems which lie outside their sphere of competence and be willing to consult other experts. In

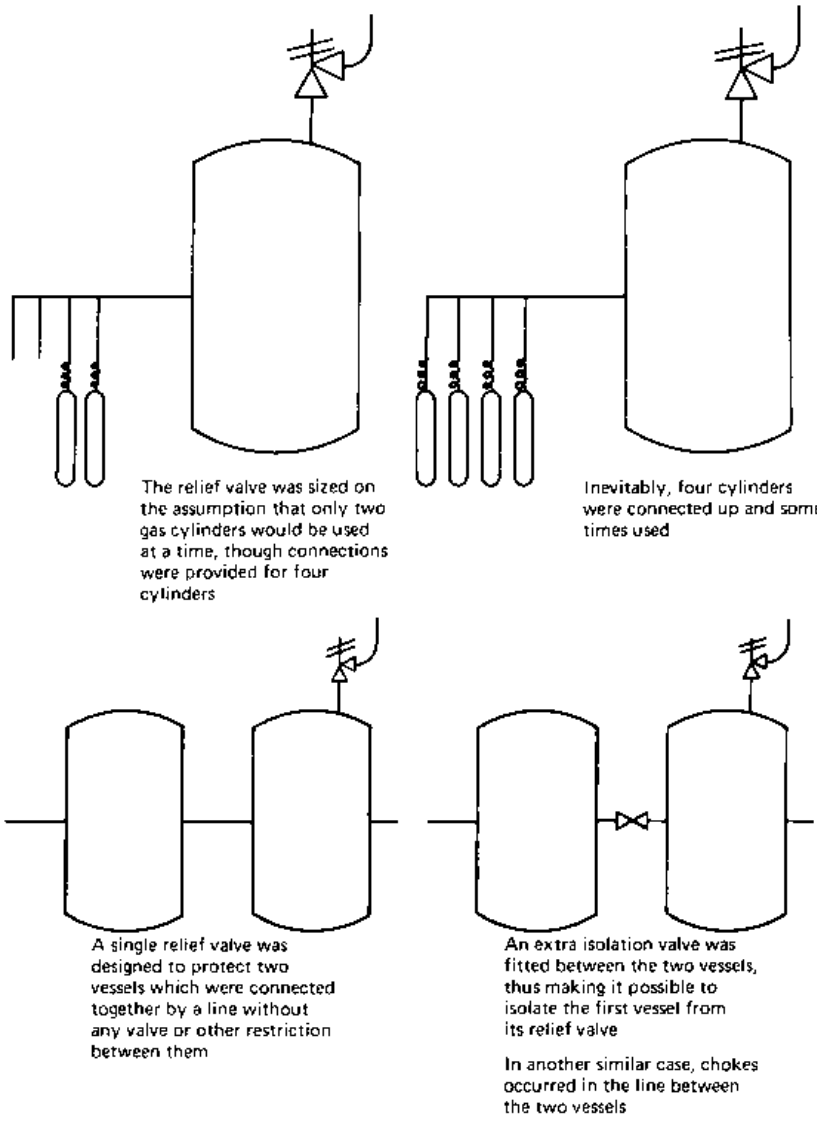


Figure 21.11 *Modifications in validating pressure relief arrangements – 3 (Henderson and Kletz, 1976) (Courtesy of the Institution of Chemical Engineers)*

effect, they should adopt the approach of the general practitioner in the medical field.

Major sanction modifications are designed in the usual way by the design departments.

21.23.2 Design authority

Some modifications require to be checked or completely designed by an appropriate design authority. There is a problem area here. Many plants are designed and built by outside contractors, who initially have the greatest expertize about the plant, but also eventually lose touch with it. There is, therefore, typically a transfer of expertize to a design authority within the operating company and often within a particular works.

21.23.3 Identification of modifications

The identification of modifications is a crucial problem. There is usually a large amount of maintenance work. It is necessary but not always easy to identify items which in fact constitute modifications. This requires that a modification be defined. The following two-part definition is given by Henderson and Kletz:

Safety Assessment

Plant **Title** **Reg no**

Underline those factors which have been changed by the proposal

Process conditions
temperature
pressure
flow
level
composition
toxicity
flash point
reaction conditions

Operating methods
start up
routine operation
shutdown
preparation for maintenance
abnormal operation
emergency operation
layout and positioning of controls & instruments

Engineering methods
trip and alarm testing
maintenance procedures
inspection
portable equipment

Safety equipment
fire fighting and detection systems
means of escape
safety equipment for personnel

Environmental conditions
liquid effluent
solid effluent
gaseous effluent
noise

Engineering hardware and design
line diagram
wiring diagram
plant layout
design pressure
design temperature
materials of construction
loads on, or strength of foundations, structures, vessels, pipework/supports/bellows
temporary or permanent pipework/supports/bellows, valves, slip-plates, restriction plates, filters
instrumentation and control systems
trips and alarms
static electricity
lightning protection
radioactivity
rate of corrosion
rate of erosion
isolation for maintenance mechanical electrical
fire protection of cables
handrails
ladders
platforms
walkways
tripping hazard
access for operation, maintenance, vehicles, plant
fire fighting
underground/overhead services, equipment

Within the categories listed below, does the proposal	Yes or no	What problem has been created which affects plant or personnel safety and what action is recommended to minimise it	Signed & date
Relief and blowdown			
1 Introduce or alter any potential cause of over/under pressuring (or raising or lowering the temperature in) the system or part of it?			
2 Introduce a risk of creating a vacuum in the system or part of it?			
3 In any way affect equipment already installed for the purpose of preventing or minimising over or under pressure?			
Area classification			
4 Introduce or alter the location of potential leaks of flammable material?			
5 Alter the chemical composition or the physical properties of the process material?			
6 Introduce new or alter existing electrical equipment?			
Safety equipment			
7 Require the provision of additional safety equipment?			
8 Affect existing safety equipment?			
Operation and design			
9 Introduce new or alter existing hardware?			
10 Require consideration of the relevant Codes of Practice and Specifications?			
11 Affect the process or equipment upstream or downstream of the change?			
12 Affect safe access for personnel and equipment, safe places of work and safe layout?			
13 Require revision of equipment inspection frequencies?			
14 Affect any existing trip or alarm system or require additional trip or alarm protection?			
15 Affect the reaction stability or controllability of the process?			
16 Affect existing operating or maintenance procedures or require new procedures?			
17 Alter the composition of, or means of disposal of effluent?			
18 Alter noise level?			

Safety Assessor **date**

Checked by **Plant Manager** **Checked by** **Engineer**

Figure 21.12 *Safety assessment form for plant modification work (Henderson and Kletz, 1976) (Courtesy of the Institution of Chemical Engineers)*

(1) Any change in the equipment, temporary or permanent, which may affect the safety of the process or safety and integrity of the plant. It does not include changes in engineering equipment which are not in contact with the process and cannot affect the safety of the process or the safety and integrity of the plant.
(2) Any change in process materials, services, operating conditions, or operating procedures, and including experimental programmes, which fall outside established practice.

The first part of this definition covers those equipment changes which are normally understood as plant modifications. The second part brings in also the process modifications.

In the system described by these authors it is the responsibility of the plant manager and plant engineer to identify modifications.

21.23.4 Critique of modifications

Modifications proposed are not always necessary. Sometimes the proposal is a symptom of a problem which is better dealt with in some other way. The technique of critical examination, described in Chapter 11 in relation to design, is applicable to modifications also. Questions which may he asked concerning a modification are: Is it necessary? Is it economic? Is there a better alternative?

21.23.5 Procedure for modifications

The procedure given by Henderson and Kletz requires that before authorizing a modification particular attention should be paid to ensuring that:

(1) The number and size of relief valves required are not changed (or any necessary changes are specified).
(2) The electrical area classification is not changed (or any necessary changes to the electrical equipment are specified).
(3) There are no effects on trips or alarms (or any necessary changes are specified).
(4) There are no other effects which might reduce the standard of safety.
(5) The appropriate engineering standards are followed.
(6) The right materials of construction and fabrication standards are used.
(7) Existing equipment is not subjected to conditions beyond the design basis without checking that it can withstand the new conditions.
(8) Any necessary changes in operating conditions are made.
(9) Adequate instruction and training are provided to operating and maintenance teams.

21.23.6 Safety assessment of modifications

The above procedures need to be supplemented by a system for the identification of hazards in the modification. The method described by Henderson and Kletz makes use of the safety assessment form shown in Figure 21.12. The form is best completed not by a single individual but by two or three people working together. The top half of the form provides check words which form the basis for a hazard and operability study and the bottom half gives a more conventional checklist.

It is found helpful in making the safety assessment to assume that, until it is shown otherwise, any isolation valve or other restriction will isolate an equipment from its protective device, e.g. a vessel from its relief valve, and that any new line will introduce some unwanted contamination, overpressure of some equipment or more flow into some equipment than its outlet pipes can handle.

This procedure, therefore, makes use of a standard form to initiate a safety assessment which goes beyond the use of a checklist.

21.23.7 Inspection of modifications

It is the responsibility of the person authorizing a modification to carry out a pre-commissioning inspection of that modification and to satisfy himself that it is in accordance with the design intent, that the standards for design, construction and testing have been followed, that the provisions of the safety assessment have been met and that the work is complete.

21.23.8 Documentation of modifications

It is essential that plant documentation be kept up to date and therefore that any modification be recorded. This requirement may be met by the use of a formal register of modifications. If the modification requires alterations to operating or inspection practices, it is necessary that the appropriate changes be made in the documentation covering these aspects.

21.23.9 Training on modification systems

A system for the control of modifications can only work if all the personnel involved are aware of and have an understanding of the system through training. The process operator who may turn off an agitator, the maintenance fitter who may blank off a vent, and the instrument artificer who may alter a trip setting all need to be aware of the hazards which these types of modification may involve and of the system of control of modifications.

The plant managers and engineers who authorize modifications need to have the theoretical knowledge, general practical experience and experience of the particular process and plant to recognize potential hazards, and also to appreciate situations where they should call in expert assistance.

21.23.10 Commissioning modifications

The commissioning stage tends to involve numerous modifications at a time when the plant manager and plant engineer are heavily loaded. It may be appropriate, therefore, to appoint special personnel to check these modifications. People who have been involved in hazard identification during the design stage may well be suitable for this task. It is also advisable to conduct a post-commissioning check of the pressure relief and blowdown arrangements about a year after start-up.

21.23.11 Variations in modification control

The system for control of modifications just outlined is essentially that described by Henderson and Kletz, and is intended primarily for larger continuous petrochemical plants. Other systems may be more appropriate for other types of plant, although the basic principles remain applicable.

21.24 Some Modification Problems

21.24.1 Design codes and standards

Like plant design, modification should be done in accordance with a standard or code of practice. Design standards or codes are not applied retrospectively to existing plant and its modification. The normal practice is to carry out modifications according to the standard or code to which the original plant was built. The exception is where the original code has been found to be seriously deficient in some way. There is, therefore, relatively little problem of retrospective application of standards and codes.

There is a problem, however, which arises from the nature of the advanced codes such as BS 5500, and earlier BS 1515, and the ASME *Boiler and Pressure Vessel Code,* Section VIII, Division 2. The design criteria in such codes are quite complex, may require analysis of stress concentration sites, of fatigue and creep, and assume finite equipment life. Design according to these codes is thus a specialist matter. It follows, therefore, that expert advice is particularly necessary for any modification to equipment designed to advanced codes. Moreover, such advice may well be required in some cases for repairs on such equipment.

21.24.2 Repair and modification codes

The main guide to the conduct of plant repairs and modifications is API RP 510: 1992 *Inspection, Rating and Repair of Pressure Vessels in Petroleum Refinery Service.* API RP 510 gives an account of its origin as a complement to the ASME *Boiler and Pressure Vessel Code* before Section VIII of the latter was split into two divisions. The ASME *Code* is written for new construction. With respect to repair or modification, RP 510 states that where due to its new construction orientation the ASME *Code* cannot be followed, RP 510 has precedence.

21.24.3 Materials aspects

The materials for modification or repair should be 'suitable' and should have properties at least equal to that of the parent material originally used. If the advanced codes apply, the materials should have guaranteed minimum properties and should be so certified. It is also necessary that both parent and replacement materials should be capable either of withstanding the fabrication processes without losing their required properties or of having these properties restored.

The availability of suitable materials may be a problem, either because a material is no longer made or because delivery times are long.

The parent material is sometimes degraded and may require treatment before welding can be done on it. Thus, for example, if there is surface sulphur contamination, it may be necessary to remove the contamination by grinding and then to preheat to allow welding. In some cases the parent metal may have been rendered unweldable by high temperature exposure or hydrogen attack.

The application of quality control procedures can give rise to difficulties. There has been continuous progress in the measurement of defects in materials and in acceptance standards. The situation can easily arise, therefore, where the quality demanded for the replacement materials far exceeds that of the original equipment material.

The properties of both parent and replacement materials may be affected by activities such as cold working, preheating or welding. Material properties may be restored to some extent by suitable heat treatment, but the heat treatment operations which can be carried out are strictly limited.

21.25 Major Plant Extensions

Major plant extensions are in large part covered by the procedures for design, on the one hand, and for modification on the other. Nevertheless, such major extension merits at least brief consideration in its own right. Reference has already been made to the British Chemical Industry Safety Council publication on plant extensions (BCISC, 1972/11). The control of major extensions is discussed by K. Wood (1971).

21.25.1 Design of modifications

A major extension involves changes on a greater scale than a normal plant modification. This means that it is particularly necessary to check on the various facilities which may become inadequate or overloaded as a result of the extension. Some features of the design which should be checked with this in mind are: (1) pressure relief valves; (2) vent, flare, blowdown and absorption systems; (3) drains and sewers; and (4) trip systems.

The design, location and capacity of the pressure relief valves should be checked and sufficient spares provided. A review should also be made of the need for liquid thermal relief on long sections of off-site pipeline which could be boxed in.

The facilities for gas and vapour relief, for flaring, for liquid blowdown and for emergency absorption should be checked.

The check on sewers and drains should cover not only the capacity of the underground sewers, but also that of the surface drainage so as to ensure disposal of fire water.

A major extension also involves more extensive changes of plant configuration. It is particularly important, therefore, to check not only that there are suitable trip systems on the extension itself, but that those on the existing plant are also still appropriate.

21.25.2 Layout for extensions

The problems of pipework during the extension should be given special attention. The number of live pipelines passing through the non-operating areas should be kept to a minimum. Despite the best safe-working procedures, incidents are frequent in which live lines are broken or burnt open by construction personnel.

Utilities lines should be isolated from the non-operating area by block valves. Sewers should also be isolated from the non-operating area, since they present the hazard that flammable gas may flow through them from the operating into the non-operating area. Wood suggests that sewers should be isolated completely rather than by the sanding down of sewer beehives.

There should be adequate provision of blanking-off points to permit pre-commissioning testing of equipment such as compressors on air or gas recycle, while

maintaining isolation of the non-operating areas from flammable gas and utilities.

21.25.3 Safe-working procedures

A major extension usually means that there are on site a large number of contractors' personnel and also additional company construction and maintenance personnel. This situation is a particularly severe test of the safe working procedures and the normal procedures should be reviewed to check that they are adequate.

The original plant usually continues in operation while construction work is in progress on the extension. It then shuts down so that it can be tied in to the expansion facilities. It is necessary to control work in the non-operating area closely, so as not to interfere with the operating plant, and it is desirable that if it is necessary to carry out gas-freeing operations on shutdown, then hot work in the non-operating area should cease until this has been done.

The permit-to-work system is usually that in normal use. But the number of permits issued is likely to increase greatly and works personnel may need to be assigned full time to analytical testing of atmospheres and issuing of permits.

In these circumstances the identification of equipment becomes even more important. Permits should specify clearly the equipment to be worked on and there should be positive identification of equipments. A colour code agreed with the contractors may be used as an additional means of identification. Pipelines in the non-operating area which are live should be clearly marked with an agreed code.

It is necessary to ensure that works and contractors' pipe blinds are kept separate. The system described by Wood is to use works blinds with a straight handle to distinguish them from the T-handle type used by contractors. Furthermore, there should be an instruction that neither party must remove the other's blinds. Incidents occur in which contractors' personnel remove blinds from live lines. As mentioned earlier, in some permit systems a separate permit is needed for the insertion or removal of blinds. This is particularly appropriate for work on major extensions.

There is need for an alarm system to cover the hazard of flammable gas release from an operating plant while hot work is being done in the non-operating area. Personnel in the non-operating area should be instructed to stop hot work when the alarm is raised. The normal alarm system should also be explained to them.

The hazard of illicit smoking should be reduced by the only effective means available, which is the provision of smoking areas.

The personnel involved in the extension should be given training on the hazards and procedures.

21.26 Notation

Section 21.6

C cleaning disturbance factor
F drag force on particle
u fluid velocity relative to particle
ρ density of fluid

Subscripts:

1 cleaning
2 operating

Section 21.20

H annual cost of holding item
P cost of procuring item
Q optimal order quantity of item
R annual requirement for item

22 Storage

Contents

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By far the largest quantities of chemicals are found in storage facilities, which may be at chemical plants or in other storage terminals. The prevention of loss in storage is therefore extremely important.

It has long been appreciated that loss of containment from storage of toxic chemicals could have particularly serious consequences. The hazard of toxic release has been considered, therefore, in some detail in Chapter 18. The hazard was realized at Bhopal, which was the worst disaster which has ever occurred in the chemical industry. A toxic release with consequences on this scale, or anything approaching it, is extremely rare and stringent measures are taken to avoid it.

Losses through fires in storage, on the other hand, constitute a major part of the losses sustained by the industry. Mostly these result in financial loss rather than loss of life and tend to make relatively little public impact. But there are exceptions such as the disasters at Feyzin, Caracas and Mexico City.

Some idea of the potential for fire loss may be obtained by considering the value represented by a single storage tank. A 'jumbo' tank might contain 500 000 barrels of oil worth US$10 per barrel and might itself be worth US$4 per barrel capacity, making a total value of US$7 million (OIA, 1975 Loss Control Bull. 400–1). Jumbo tanks of from 300 000 to 1 000 000 barrels capacity are currently being used to store not only crude oil but also flammable intermediate and finished products.

Storage is one of the areas in which there is a good deal of legislation. This was described in Chapter 3.

Much storage is sited in or near urban areas. It is generally reckoned to be relatively safe and unlikely to cause large loss of life, but it is nevertheless a source of some public concern. There is, therefore, the problem of siting and of the relation between siting and preventive measures. This aspect is considered in Chapter 4. Storage is frequently one of the topics dealt with under the headings of plant siting and layout, and some aspects of storage have been considered in Chapter 10.

The location of storage in relation to the process is also important. Storage is most likely to be put at risk by a process. It is necessary, therefore, for the two to be segregated. This reduces the risk of a process incident hazarding the very large inventory in storage. It also makes it less likely that a minor incident in storage will put the process at risk.

There are numerous standards and codes of practice which are applicable to storage. The treatment of storage given here attempts to outline some of the principles described in the codes. There are differences, however, between codes and there are critics of the codes, and some of these points are mentioned also. The practices described should be regarded only as typical. In particular, the codes themselves should be used for design work.

Safety in storage is as much a matter of operation and maintenance as of design. Some aspects of operation and maintenance of storage were discussed in Chapters 20 and 21, respectively.

Good operation and maintenance depend on an effective management system. While it should be possible to assume that such a system exists in a large chemical works, there is potentially a problem in situations where products such as liquefied petroleum gas (LPG) or chlorine are stored and used in non-chemical and low technology industries. In this case a particular responsibility rests on the supplier of the chemical to advise the user.

There is no UK code specifically for the storage of chemicals in general except insofar as these are covered by codes for petroleum products, flammable liquids, LPG and liquefied flammable gas (LFG), but there are codes for a number of individual chemicals.

The treatment given here deals in turn with the storage of flammable materials, the storage of toxic materials, loading and unloading facilities, drum and cylinder storage, and warehouses. It also describes case histories and hazard assessments of storage.

Selected references on storage of hazardous materials are given in Table 22.1.

Table 22.1 *Selected references on the storage of hazardous materials*

ACGIH (n.d./4, 1987/15); NFPA (Appendix 27, 1990 NFPA 231); Aldrich (1960a,b); Grover and Wilson (1960); Hower (1961); Leach (1962); Duggan (1964b); Fuller and Bristline (1964); Risinger (1964h); Zick and Clapp (1964); Hughson (1965); IP (1980 Eur. MCSP Pt 2, 1981 MCSP Pt 3, 1987 MCSP Pt 9); Redington (1965); Voegelen (1965); IChemE (1966/44); FMEC (1967); Salot (1967); Wardale and Todd (1967); Cotton and Denham (1968); Denham, Russell and Wills (1968); Home Office (1968/1, 1971/2); Zick and McGrath (1968); D.M. Johnson (1969); Boberg (1970); FPA (1970/12, 1972/17, 1989 FS 6011, 6012); Hearfield (1970); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); J.S. Clarke (1971); Simpson (1971); McGrath (1973, 1975, 1976); Mecklenburgh (1973, 1976, 1985); R.C. Ross (1973); Shinnar (1973); Vervalin (1973a,f); Chicago Bridge and Iron Co. (1974, 1975a,b, 1976a,b); Unwin, Robins and Page (1974); Walsham (1974); OIA (1975 Loss Control Bull. 400-2); HSE (1977 CS/2); Wafelman and Burhmann (1977); Ghali (1979); Santi (1979); Malina (1980); API (1981 *Refinery Guide* Ch. 13, 1982/5, 1984 Publ. 2008, 1990 Std 620, 1993 Std 650); Burk (1981); Anon. (1982 LPB 47, p. 26); Doi and Osawa (1983); Gallagher (1983); Giger, Gygax and Hoch (1983); Petherbridge and Kinder (1983); Prieto (1985); Ackermann (1986); AIChE (1986/85); Anon. (1987w); Frey and Handman (1987); Sims (1987); Nazario (1988); ILO (1989); Sanders, Haines and Wood (1990); Seton, Fitterer and Harris (1992); Bartlett, Hall and Gudde (1993); Rorty and McLearn (1993); Shah, Shah and Mody (1993); ANSI MH5.1.3M-1982
BS (Appendix 27 *Pressure and Other Vessels*), BS 4994: 1987

Low temperature storage
H.V. Bell (1982); Pieper, Zick and Fave (1982); Aarts and Morrison (1981); EEMUA (1986 Publ. 147); CGA (1987 CGA-341); Anon. (1988 LPB 79, p. 25)
BS 4741: 1971, BS 5387: 1976

High temperature storage
Karcher (1978, 1981)

Atmospheric tanks (see also *Particular chemicals*, below)
Ulm (1963); Zick and McGrath (1968); Anon. (1975 LPB 0, p. 3); McGrath (1976); CIA (1978/11); H.I. Epstein and Buzek (1978); Morgenegg (1978); Anon. (1980 LPB 32, p. 1); Winegar (1980); G. Allen (1984); API (1985/15, 1990 Std 620, 1993 Std 650); C. Clark (1987); Kletz (1988m); ASME (1989 B96.1); IGasE (IGE/SR/7); HSE (1991 HS(G) 52); Hassan (1992); W.B. Howard (1992a); BS 799 Pt 5: 1987, BS 2654: 1989
Overfill protection: API (1987 RP 2350)
Tank stability, collapse: McGrath (1963); Anon. (1975 LPB 0, p. 3); Cuperus (1979, 1980); Skowronski (1980); Winegar (1980); Anon. (1981 LPB 37, p. 1); J.C. Thompson (1985); Anon. (1988m); Trbojevic and Gjerstad (1989); Trbojevic and Slater (1989); Neville and White (1991); Peters and Hansel (1992)
Layering, rollover. Chatterjee and Geist (1972); Sarsten (1972); Drake, Geist and Smith (1973); Germeles (1975a,b); Drake (1976); Bellus *et al.* (1977); Anon. (1979 LPB 29, p. 124); Heestand, Shipman and Meader (1983); Nakano *et al.* (1983); Takao and Suzuki (1983); Anon. (1992 LPB 107, p. 1)

Tank foundations, settling
W.W. Moore (1963); Rinne (1963); Morrison and Marshall (1970); C.C. Hale (1974); Esrig, Ahmad and Mayo (1975); Comeau and Weber (1977); Lichtenberg (1977); BRE (1978 CP14/78); Vick, Witthaus and Mayo (1980); Russo and Haydel (1983); Martinez, Madhavan and Kellett (1987)

Tank linings
Sumbry and Bogner (1993)

Concrete storage tanks
E.L. Smith (1966); Edmondson (1984 LPB 54)

Secondary containments, bunds
Comeau (1972); MacArthur (1972); C.C. Hale (1974); J.D. Reed (1974); CIA (1975/8); Anon. (1978 LPB 24, p. 164); Anon. (1979 LPB 26, p. 52); Koerner and Lord (1987); Barnes (1990 SRD R500); FPA (1990 CFSD FS 6027); Wilkinson (1991 SRD R530); Rakoczynski and Long (1993)
Bund overflow: Greenspan and Young (1978); Greenspan and Johansson (1981); Michels, Richardson and Sharifi (1988); Barnes (1990 SRD R500); Wilkinson (1991 SRD R530)
Impounding basins: Roopchand and Moderegger (1993)

Vents, reliefs, flame arresters
Cinnamon and Myers (1965); HSE (1965 HSW Bklt 34); API (1966 Bull. 2521, 1982 PSD 2210, 1988– RP 520, 1990 RP 521, 1991 Publ. 2028, 1992 Std 2000); Anon. (1972k); G.F. Bright (1972); Cude (1974a,b); Gustin and Novacek (1979); Anon. (1980 LPB 36, p. 1); Gerardu (1981); Anon. (1986 LPB 72, p. 1); Förster, Schampel and Steen (1986); Kletz (1986 LPB 67); Leung *et al.* (1988); W.B. Howard (1992a,b); NFPA (1994 NFPA 68)

Evaporation, vapour recovery
Zabaga (1980); Beychok (1983); Laverman (1984); Rapp (1984); Durr and van Laerhoven (1985)

Tank inerting
Kletz (1971); Craven (1975); Förster, Schampel and Steen (1986); W.B. Howard (1992a)

Tank insulation
Leach (1962); Adorjian, Crawford and Handman (1982); Huther, Zehri and Anslot (1985); Kaups (1985); Krause (1985)
Heat gain, loss: Falicoff and Popovich (1981); Kumana and Kothari (1982); Scheirman and Rogers (1985)

Tank farms
D.M. Johnson (1969); OIA (1975 Loss Control Bull. 400-2); Burk (1981); Ahmed (1984)

Gas storage, gasholders
IGasE (n.d./l, 1986 IGE/SR/14)

Above ground storage
AGA (1981/37, 1986/47); UL (1987 UL 142); API (1991 RP 651, 652, Publ. 301)
Leak detection: API (1991 Publ. 306, 307)

Underground storage
Scisson (1969); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); Sherman (1970); Temple (1973); Beam and Giovannetti (1975); Weismantel (1978); Dwyer (1985); UL (1985 UL 58, 1986 UL 1316); Russell and Hart (1987); Schwendeman and Wilcox (1987); K.W. Brown and Thomas (1988); Haxo (1988); Anon. (1989c); Darilek and Parra (1989); Higgins and Byers (1989); E. Johnson (1989a); Lindblom (1989); Semonelli (1990); Chidambariah *et al.* (1991); Bellani, Cannalire and Beltrame (1992); Geyer (1992); NFPA (1992 NFPA 328, 329); IBC (1993/107); Maresca *et al.* (1993); J.E. Robinson (1993)

In-ground barriers
API (Publ. 315); Khinnavar *et al.* (1991)

Frozen earth storage
Massey (1964); Ferguson (1975); HSE (1978b, 1981a); Boulanger and Luyten (1983a,b)

Loading and unloading facilties
OIA (Publ. 711); Herzog, Ballard and Hartung (1964); ICI/RoSPA (1970 IS/74); API (1975 Bull. 1003); Houghton, Simmons and Gonso (1976); Anon. (1977 LPB 15, p. 2); Rees (1981); Ackermann (1986); Lichtenberg (1987); Anon. (1992 LPB 103, p. 24)
Hoses: CGA (1983 TB-3, 1985 P-7); UL (1984 UL 536, 1985 UL 1, 1986 UL 21); BS (Appendix 27 *Hoses and Hose Couplings*)

Filling ratios
ICI/RoSPA (1970 IS/74) BS 5355: 1976

Marine terminals
J.R. Hughes (1970); NFPA (1990 NFPA 307)

Container storage
HSE (1991 HS(G) 51); NFPA (1993 NFPA 55)
Drum storage: Anon. (1979 LPB 27, p. 68); Anon. (1979 LPB 28, p. 115); Anon. (1985cc)
Intermediate bulk container storage: Spivey (1992)

Cylinder storage: Home Office (1973/4); Anon. (1978 LPB 20, p. 45); BCGA (1988 GN2)

Warehouses (*see also* Tables 16.1 and 16.2)
FPA (1970/9, 13); HSE (1971 HSW Bklt 47); Mecklenburgh (1973, 1985); CIA (1983 RC28); Sims (1987); Heels (1988 LPB 84); C.R. Pearson (1988); Anon. (1989 LPB 88, p. 9); HSE (1991 HS(G) 64, 1992 HS(G) 71); NFPA (1991 NFPA 231C); R. Gibson (1992); ANSI MH21.1-1974

Fire, explosion (*see also* Table 16.2)
Vervalin (1964a, 1973a); Hearfield (1970); Simpson (1971); Kovacs and Honti (1974); OIA (1974 Loss Inf. Bull. 400-1); R.B. Robertson (1976b); Kobori, Handa and Yumoto (1981); Fauske (1989b)

Fire protection (*see also* Table 16.2)
FPA (S9, 1986 CFSD GP 7, 1988 CFSD GP 6); Bray (1964, 1966); Allinson (1966); Chaillot (1966); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); Kletz (1971, 1974e, 1975b,d, 1976g, 1977d); Craven (1975); Zuber (1976); Anon. (1978 LPB 20, p. 20); Anon. (1978 LPB 22, p. 114); Blything (1983 SRD R263); British Gas (1984 BGC/PS/SFP1); Williams (1984); Raine (1986); Fullam (1987); IBC (1988/75); Nazario (1988); Schoen and Droste (1988); Schoen, Probst and Droste (1989); NFPA (1993/34); BS 5908: 1990
Insulation: Feind (1978); Katzler (1980); Uppal (1980); Anon. (1985q)

Particular chemicals
Ammonia (anhydrous): American Oil Co. (n.d./9); HSE (HS(G) 30); W.L. Nelson (1948); T.J. Dawson (1956); Jenkins (1962); Applegate (1965); Crowley (1965); Husa and Bulkley (1965); Laing and Henderson (1965); G.O. Morgan and Reed (1965); Eddy, Schroedter and Strauch (1966); J.A. Lawrence (1966); Hoffman (1967); Resplandy (1967); W.L. Ball (1968b); Scisson (1969); Morrison and Marshall (1970); A. Nielsen (1971); Comeau (1972); Lichtenberg (1972); MacArthur (1972); C.C. Hale (1974, 1980, 1982, 1984, 1987); J.D. Reed (1974); Vidalin and Bertram (1974); CIA (1975/8); Esrig, Ahmad and Mayo (1975); Lonsdale (1975); van Grieken (1976); Arup (1977); Comeau and Weber (1977); Feind (1978); Truscott and Livingstone (1978); Gustin and Novacek (1979); C.C. Hale and Lichtenberg (1980, 1990); Hendriks (1980); Vick, Witthaus and Mayo (1980); Winegar (1980); Aarts and Morrison (1981); Blanken (1982, 1984, 1987); R.S. Brown (1982); Shah (1982); Anon. (1984 LPB 58, p. 13); Guth and Clark (1985); Badame (1986); P.P. Briggs, Richards and Fiesinger (1986); Josefson (1987); Shah (1987); J.L. Woodward and Silvestro (1988); Stephens and Vidalin (1988); Byrne, Moir and Williams (1989); CGA (1989 TB-2); ILO (1989); W.G. Jones *et al.* (1989); J.R. Thompson and Carnegie (1989); Appl *et al.* (1990); Burke and Moore (1990); Selva and Heuser (1990); J.H. Thompson (1990); Conley, Angelsen and Williams (1991); Squire (1991); Herbertsson (1992); Tilton *et al.* (1992); ANSI K61.1–1989
Ammonia (aqueous): Henderson (1975)
Asphalt, bitumen: API (1988 Publ. 2023); IP (1990 MCSP Pt 11); Davie, Nolan and Hoban (1993, 1994); Davie *et al.* (1993); Davie, Nolan and Tucker (1993)
Chlorine: BCISC (n.d./1); HSE (HSW Bklt 37, 1985 CS 16, 1986 HS(G) 28, 1987 HS(G) 40); CIA (1980/13); Chlorine Institute (1982 Pmphlt 5, 1986 Pmphlt 1); ILO (1989)
Hydrogen: A.D. Little (1960); Vander Arend (1961); Cassut, Madocks and Sawyer (1964); Scharle (1965); Stoll (1965); Angus (1984); NFPA (1989 NFC 50A, 50B)
LNG (*see* Table 11.23)
LPG (*see also* Table 11.22): IGasE (n.d./5); FPA (1964/1); Sommer (1965); J.R. Hughes (1970); ICI/RoSPA (1970 IS/74); Home Office (1971/2, 1981 HS(G) 15, 1987 HS(G) 34); LPGITA (1972– Codes 1, 3, 7, 9, 12, 14, 19, 22); Considine, Grint and Holden (1982); HSE (1973 Bklt 30, 1981 CS 5,CS 6, 1986 CS 4); Blything (1983 SRD R263, 1986); Lindblom and Quast (1983); Nozaki *et al.* (1983); I. Williams (1984); Howell and Schuller (1985); Morand, Claude and Herbreteau (1985); Sugawara and Minegishi (1985); Ackermann (1986); Davenport (1986, 1988); van der Schaaf (1986); IP (1987 MCSP Pt 9); Blomquist (1988); API (1989 Std 2510); Droste and Mallon (1989); ILO (1989); Lindblom (1989); NFPA (1992 NFPA 58, 59); Paff (1993); British Gas (1994 GBE/DAT27)
Monomers (see also *Styrene monomer and Vinyl chloride monomer,* below): Shelley and Sills (1969); Bond (1985 LPB 65); Anon. (1992 LPB 106, p. 14); Chakravarty, Fisher and Voyt (1993)
Petroleum: H. Watts (1951); Home Office (1968/1); J.R. Hughes (1970); IP (1990 Eur. MCSP Pt 2, 1981 MCSP Pt 3)

Particular chemicals: other chemicals
Acrylic acid: Wampler (1988)
Ammonium nitrate: American Oil Co. (n.d./9); HSE (1986 CS 18); NFPA (1993 NFC 490)
Carbon dioxide: HSE (1985 CS 9); Coleman (1989)
Corrosive chemicals: Anon. (1977 LPB 16, p. 21); Anon. (1979 LPB 26, p. 31)
Ethylene: Litchfield *et al.* (1959); Frank and Wardale (1970); Wardale and Frank (1970); Anon. (1985q)
Ethylene oxide: CISHC (1975/2); Curtis (1990)
Explosives: Home Office (1972/3)
Hydrogen chloride: BCISC (1975/2)
Liquefied gas: Dharmadhikari and Heck (1991)
Organic peroxides: HSE (1991 CS 21); NFPA (1993 NFPA 43B)
Oxidizing materials: NFPA (1986 NFPA 43C, 1990 NFPA 43A)
Oxygen: HSE (1977a); NFPA (1990 NFC 50)
Plastics, plastic foams: MCA (SG-5); HSE (1975 TDN 29)
Shock sensitive materials: MCA (SG-7)
Sodium chlorate: HSE (1985 CS 3)
Styrene monomer: Shelley and Sills (1969)
Toxic chemicals: Ecology and Environment Inc. (1985); Croce *et al.* (1988); Drake and Croce (1988)
Vinyl chloride monomer: Shelley and Sills (1969); Unwin, Robins and Page (1974); Mukerji (1977); CIA (1978/12)

Hazard assessment (*see also* Table 9.1)
Husa and Bulkley (1965); Resplandy (1967); Siccama (1973); Solomon, Rubin and Okrent (1976); HSE (1978b, 1981a); Drysdale and David (1979/80); Considine, Grint

and Holden (1982); R. Davies (1982); Suokas (1982); Drivas, Sabnis and Teuscher (1983); Lees (1983d); T.A. Smith (1985, 1986 SRD R314); Trbojevic and Maini (1985); Blything (1986); Blything and Reeves (1988 SRD R488); Clay *et al.* (1988); Selway (1988 SRD R492); Smith-Hansen (1988); Boykin and Levary (1989); Ziomas, Zerefos and Bais (1989); Haastrup and Brockhoff (1990); Khan (1990); P. Roberts (1990); Chidambariah *et al.* (1991); Nejedly, Topinka and Skarka (1992)

22.1 General Considerations

22.1.1 Purpose of storage

The purpose of storage is to smooth fluctuations in the flows in and out. If the quantity in stock does not vary, there is no point in having storage. The exception is where the storage is held purely as an insurance.

Thus there may be various ways of satisfying the design objective. The types of storage which are

Table 22.2 *Some principal hazardous events and initiating events for storage*

A Hazardous events

Materials	*State*	*Storage*	*Hazardous events*
Flammable	Liquid	Atmospheric	Liquid release, then Tank or bund fire Tank explosion, then Tank or bund fire
	Liquefied gas	Pressure	Flashing liquid release – flammable vapour cloud, liquid pool, then Pool fire Running liquid fire Jet fire Vapour cloud fire Vapour cloud explosion Fire engulfed vessel, then Jet fire BLEVE
	Liquefied gas	Refrigerated	Flashing liquid release – flammable vapour cloud, liquid pool, then Tank or bund pool fire Running liquid fire Vapour cloud fire Vapour cloud explosion Fire engulfed tank, then Tank or bund pool fire Running fire
Toxic	Liquid	Atmospheric	Liquid release, then Toxic gas cloud Tank explosion, then Toxic gas cloud
	Liquefied gas	Pressure	Flashing liquid release – flammable vapour cloud, liquid pool, then Toxic gas cloud Fire engulfed vessel, then BLEVE Toxic gas cloud
	Liquefied gas	Refrigerated	Flashing liquid release – flammable vapour cloud, liquid pool, then Toxic gas cloud Fire engulfed tank, then Toxic gas cloud

B Initiating events

Catastrophic failure of vessel or tank
Failure of or leak from other equipment, pipework or fittings
Explosion in vessel or tank
Fire engulfing vessel or tank
Jet flame playing on vessel or tank
Overfilling of vessel or tank
Release occasioned by operations
Release occasioned by maintenance
Impact event
Natural event
Arson, sabotage

economic in these alternative designs may be different and may have different safety implications also. There may be considerable differences, for example, in the pressure and in the inventory. An account which illustrates the interaction between storage requirements and storage method is given by Hower (1961).

22.1.2 Storage conditions

The main sets of conditions for gas or liquid storage are

(1) liquid at atmospheric pressure and temperature (atmospheric storage);
(2) liquefied gas under pressure and at atmospheric temperature (pressure storage);
(3) liquefied gas under pressure and at low temperature (refrigerated pressure storage, semi-refrigerated storage);
(4) liquefied gas at atmospheric pressure and at low temperature (fully refrigerated storage);
(5) gas under pressure.

The fluids so stored are referred to for convenience as (1) volatile liquids, (2) flashing liquefied gases, (3) semi-refrigerated liquefied gases, (4) refrigerated liquefied gases and (5) gases under pressure, respectively.

The characteristics of these different types of storage have been discussed in Chapter 15. A leak of volatile liquid held at atmospheric temperature and pressure results only in a relatively slow evaporation of the liquid. Escape of a refrigerated liquefied gas at atmospheric pressure gives some initial flash-off and then an evaporation which is relatively slow but faster than the first case. Loss of containment of a liquefied gas under pressure and at atmospheric temperature, however, causes immediate flashing of a large proportion of the gas, followed by a slower evaporation of any residue, and is usually much the most serious case. The hazard from a gas under pressure is normally much less in terms of the amount of material held, but the physical energy released if a confined explosion occurs is large.

The economics of storage of liquefied gases are that it is usually attractive to use pressure storage for small quantities, pressure or semi-refrigerated storage for medium to large quantities and fully refrigerated storage for very large quantities.

It is generally considered, however, that there is a greater hazard in storing large quantities of liquefied gas under pressure than at low temperature, so that the trend is towards replacing pressure storage by refrigerated storage for large inventories.

22.1.3 Storage capacity

Methods of the estimation of the capacity of particular types of tank or vessel are given by Santi (1979) and Gallagher (1983).

22.1.4 Storage hazards

The hazards presented by storage depend on the material and on the type of storage. In broad terms, the principal hazardous events are as shown in Table 22.2, Section A. Some principal initiating events are given in Section B of the table.

On very rare occasions a vessel or tank fails catastrophically. This may occur due to mechanical or metallurgical defects. The vessel or tank may be overpressured by overfilling. A tank may be overpressured by too rapid filling and underpressured by too rapid emptying. Other causes of tank failure are given in Chapter 20.

More commonly, release occurs from other equipment or from pipework or fittings. Equipment which may leak includes, in particular, pumps. Release from pipework may occur due to a crack or pinhole or by full bore rupture, or by a leak or failure at a flange, gasket or valve.

Release may occur due to an explosion in the tank or vessel. There are various ways in which this can happen. One is physical overpressure which causes the vessel or tank to burst. Another is the ignition of a flammable mixture. Another is evolution of gas due to the reaction of an impurity, material of construction, etc. A fourth is a runaway reaction within the vessel or tank.

Fire at a vessel or tank can cause it to fail. The fire may be a fire beneath it or a jet flame playing on it.

An operational activity which may cause either direct release or vessel or tank rupture is overfilling. Other operational events which may give rise to a release include draining and sampling operations. Maintenance activities may result in a release, generally by admission of fluid to a section which is not fully isolated.

Impact events which may cause loss of containment from a storage include impact from a carried item, a dropped load, a vehicle, or an aircraft. A missile from an explosion is another form of impact, but is primarily an escalating rather than a true initiating event.

Natural events which may cause loss of containment include high winds, rainstorms, flooding, tsunamis and earthquakes, whilst lightning may start a fire.

Arson or sabotage are other causes of hazardous events. Sabotage may take the form of interference with the plant or direct initiation by impact, fire or explosion.

22.2 Petroleum Products Storage

It is convenient to start with a consideration of the storage used in the oil industry for crude oil and petroleum products.

There exist a number of standards and codes for the storage of petroleum products and flammable liquids generally. Standards and codes include API Std 620: 1990 *Design and Construction of Large, Welded, Low-pressure Storage Tanks* and Std 650: 1988 *Welded Steel Tanks for Oil Storage*, NPFA 30: 1990 *Flammable and Combustible Liquids Code* and the *Refining Safety Code* of the IP (1981 MSCP Pt 3). HSE guidance is given in HS(G) 50 *The Storage of Flammable Liquids in Fixed Tanks (up to 10,000 m^3 Total Capacity)* (1990) and HS(G) 52 *The Storage of Flammable Liquids in Fixed Tanks (Exceeding 10,000 m^3 Capacity*) (1991).

Storage of petroleum is discussed here under the following headings:

(1) storage tanks and vessels;
(2) storage layout;
(3) venting and relief;
(4) fire prevention and protection.

These are now considered in turn.

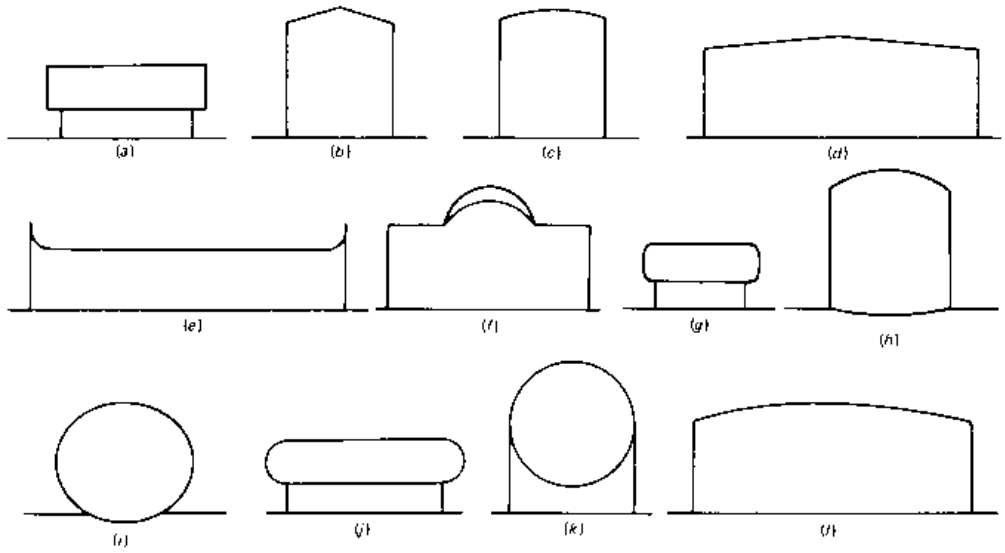


Figure 22.1 *Storage tanks and vessels: (a) horizontal cylindrical atmospheric tank; (b) vertical fixed roof atmospheric tank (coned roof); (c) vertical fixed roof atmospheric tank (domed roof); (d) vertical fixed roof atmospheric tank (large coned roof); (e) vertical floating roof atmospheric tank; (f) vapour dome atmospheric tank; (g) horizontal cylindrical low pressure tank; (h) vertical cylindrical hemispheroidal low pressure tank; (i) spheroidal low pressure tank; (j) horizontal cylindrical pressure vessel; (k) spherical pressure vessel (Horton sphere); (l) vertical fixed roof refrigerated atmospheric tank (domed roof)*

22.3 Storage Tanks and Vessels

The main types of storage tanks and vessels for liquids and liquefied gases are (1) atmospheric storage tanks, (2) low pressure storage tanks, (3) pressure or refrigerated pressure storage vessels, and (4) refrigerated storage tanks.

The API standards for storage tanks are API Std 620: 1990 *Design and Construction of Large, Welded, Low-pressure Storage Tanks* and Std 650: 1988 *Welded Steel Tanks for Oil Storage*. Relevant British Standards are BS 2594: 1975 *Specification for Carbon Steel Welded Horizontal Cylindrical Storage Tanks* and BS 2654: 1989 *Specification for Manufacture of Vertical Steel Welded Non-refrigerated Storage Tanks with Butt-welded Shells for the Petroleum Industry*.

Some of the main types of storage tanks and vessels are shown schematically in Figure 22.1 and are illustrated in Figures 22.2–22.5. Fuller descriptions and illustrations of storage tanks and vessels are available in various sources (e.g. J.R. Hughes, 1970; API, 1981 *Refinery Inspection Guide*, Ch. 13; HSE, 1973 HSW Bklt 30). Tanks and vessels for the storage of LPG, liquefied natural gas (LNG), ammonia and chlorine are considered further below.

22.3.1 Atmospheric storage

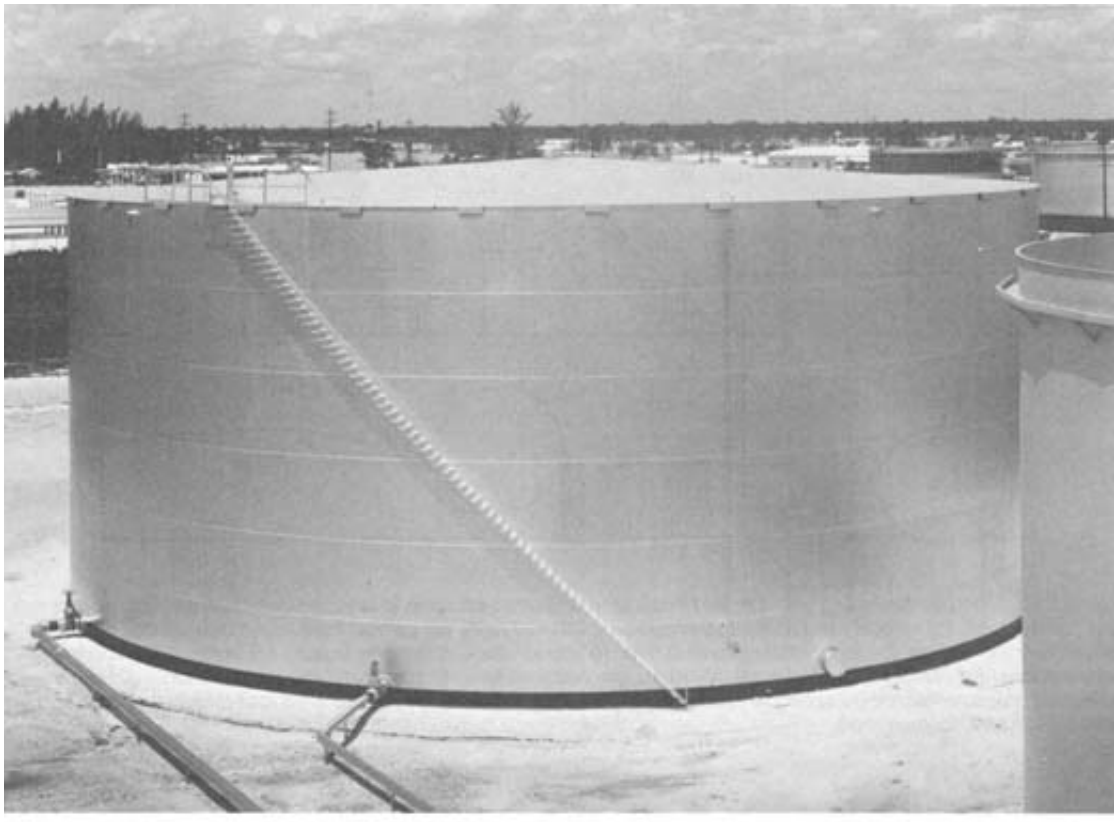
Some typical atmospheric storage tanks are shown in Figures 22.1(a–f). Figure 22.1(a) is a horizontal cylindrical tank. These tanks usually have riveted flat or welded dished ends. Figures 22.1(b) and 22.1(c) are vertical cylindrical fixed tanks with coned and domed roofs, respectively. Figures 22.1(d) and 22.1(e) are, respectively, another larger fixed roof tank and a large floating roof tank. Figure 22.1(f) is a vapour dome tank with a flexible diaphragm in the dome.

Atmospheric tanks are designed to withstand an internal pressure/vacuum of not more than 1 psig (70 mbar). Further details are given below.

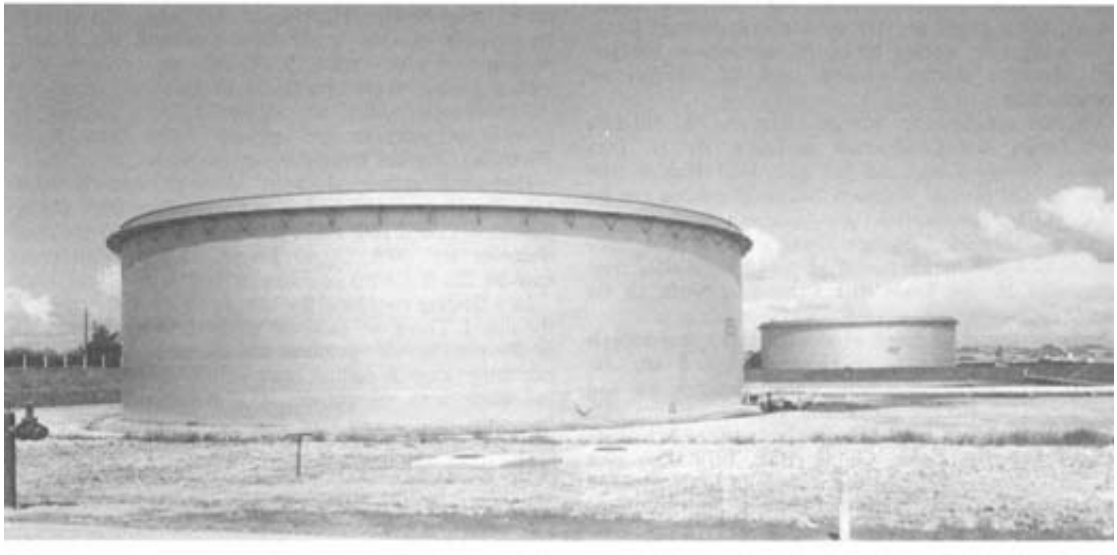
Horizontal cylindrical tanks have a relatively small capacity. Domed roof tanks go up to about 60 ft (20 m) diameter. Coned roof tanks are built up to 250 ft (76 m) diameter and 60 ft (20 m) height. Floating roof tanks may be 250 ft (76 m) in diameter and 72 ft (22 m) high.

In a floating roof tank the roof floats on the surface of the liquid. There are different kinds of floating roof such as the pan, annular pontoon and double-deck types. The two latter have a double layer at the annulus and over the whole area, respectively, and therefore have greater buoyancy than a pan roof. Sealing between the floating roof and the tank wall is effected by a number of means such as spring-loaded fabric or rubber tube seals. In addition, a floating deck may also be used inside a fixed roof tank. Its main purpose is the reduction of vapour loss.

A traditional divide between the different sizes of storage tank is a nominal capacity of 12 000 UKgal (55 m^3), which has corresponded to the approximate limit of shop fabrication. The design of petroleum storage tanks up to this capacity is governed by BS 799: 1972–



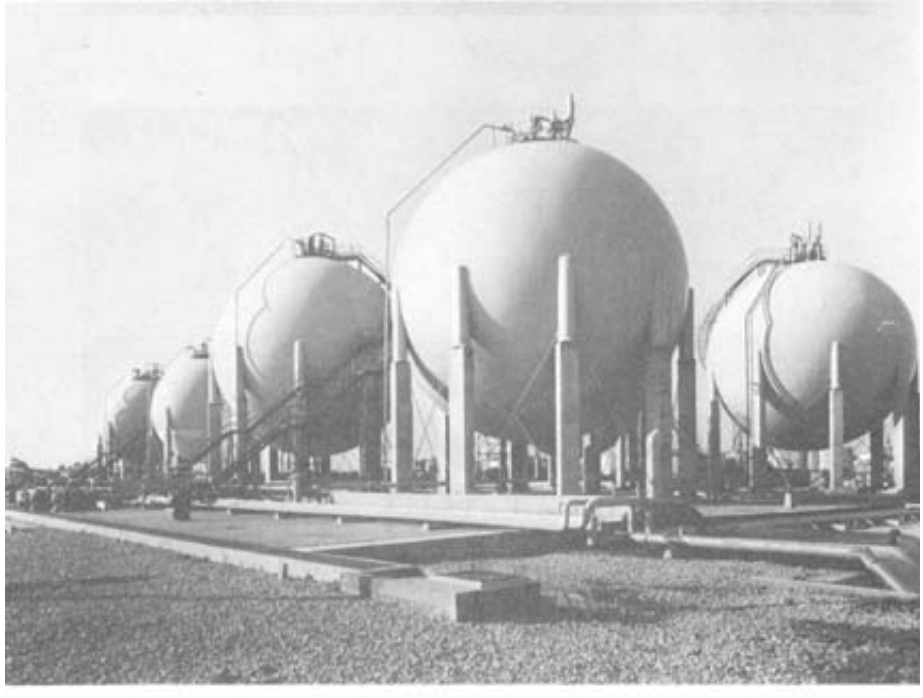
(*a*)



(*b*)

Figure 22.2 *Atmospheric storage tanks (Chicago Bridge and Iron Co.): (a) cone roof tank; (b) floating roof tank*

(*a*)



(*b*)

Figure 22.3 *Pressure storage vessels: (a) horizontal cylindrical vessels for LPG (Health and Safety Executive); (b) spherical vessels for liquid propane/butane (Horton spheres) (Whessoe Ltd)*

(a)

(b)

Figure 22.4 *Large storage complexes, including: (a) cone roof and floating roof tanks and spherical pressure vessels (Chicago Bridge and Iron Co.); (b) cone roof tanks, spheroidal vessels and cylindrical pressure vessels (Chicago Bridge and Iron Co.)*

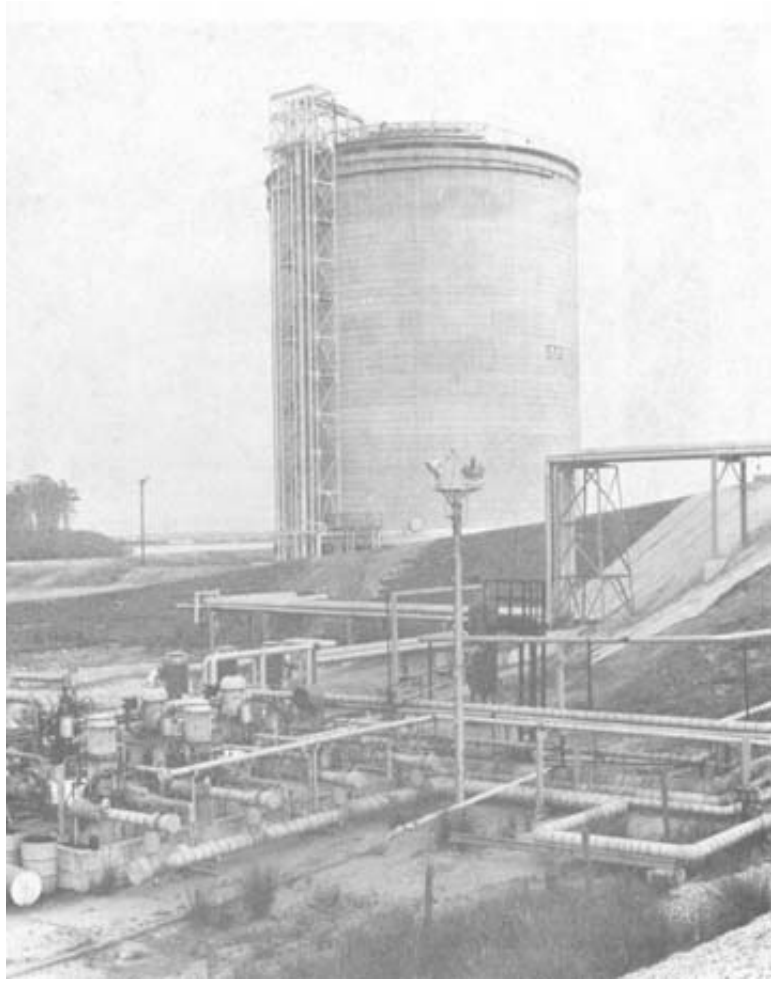


Figure 22.5(a) *Refrigerated atmospheric storage tank for liquid propane (Whessoe Ltd)*

Oil Burning Equipment. Another applicable standard is BS 2594: 1975, which covers tank sizes both below and above 12 000 UKgal.

Large petroleum storage tanks are normally site erected and of mild steel welded construction. The design, fabrication, erection, inspection and testing of these tanks is specified in API Std 650: 1988 and BS 2654: 1989.

For fixed roof tanks a traditional distinction (see BS 2654: 1961; J.R. Hughes, 1970) has been between 'non-pressure' and 'pressure' tanks. For tanks up to 128 ft diameter, non-pressure tanks were designed for an internal pressure of 3 in. WG (7.5 mbar) and a vacuum of $2\frac{1}{2}$ in. WG (6 mbar) and pressure tanks for an internal pressure of 8 in. WG (20 mbar) and $2\frac{1}{2}$ in. WG (6 mbar) plus superimposed load. The user was allowed to specify, however, an internal pressure greater than 8 in. WG. Pressure tanks up to 64 ft could be designed up to $21\frac{1}{2}$ in. WG (54 mbar) provided the allowable stress did not exceed that given in the standard.

The designation of atmospheric storage tanks with a design pressure well below 1 psig as 'pressure' tanks is a possible source of confusion. As described below, there are other tanks designed for the low pressure range 0.5–15 psig which are termed 'low pressure'.

Non-pressure tanks are normally vented by an atmospheric vent and pressure tanks by a breather vent, as described below. Non-pressure tanks tend to have relatively high vapour losses from the 'breathing' of the vent. Pressure tanks with breather vents reduce these losses but are limited in diameter. Floating roof tanks provide an alternative which has low vapour losses and is available in large sizes.

The definitions of storage tanks now recognized in BS 2654: 1989 are somewhat different. The standards defines three categories of tank: (1) 'non-pressure' tanks designed for an internal pressure of 7.5 mbar (4 mbar for column-supported roofs) and a vacuum of 2.5 mbar; (2) 'low-pressure' tanks designed for an internal pressure of 20 mbar and a vacuum of 6 mbar; and (3)

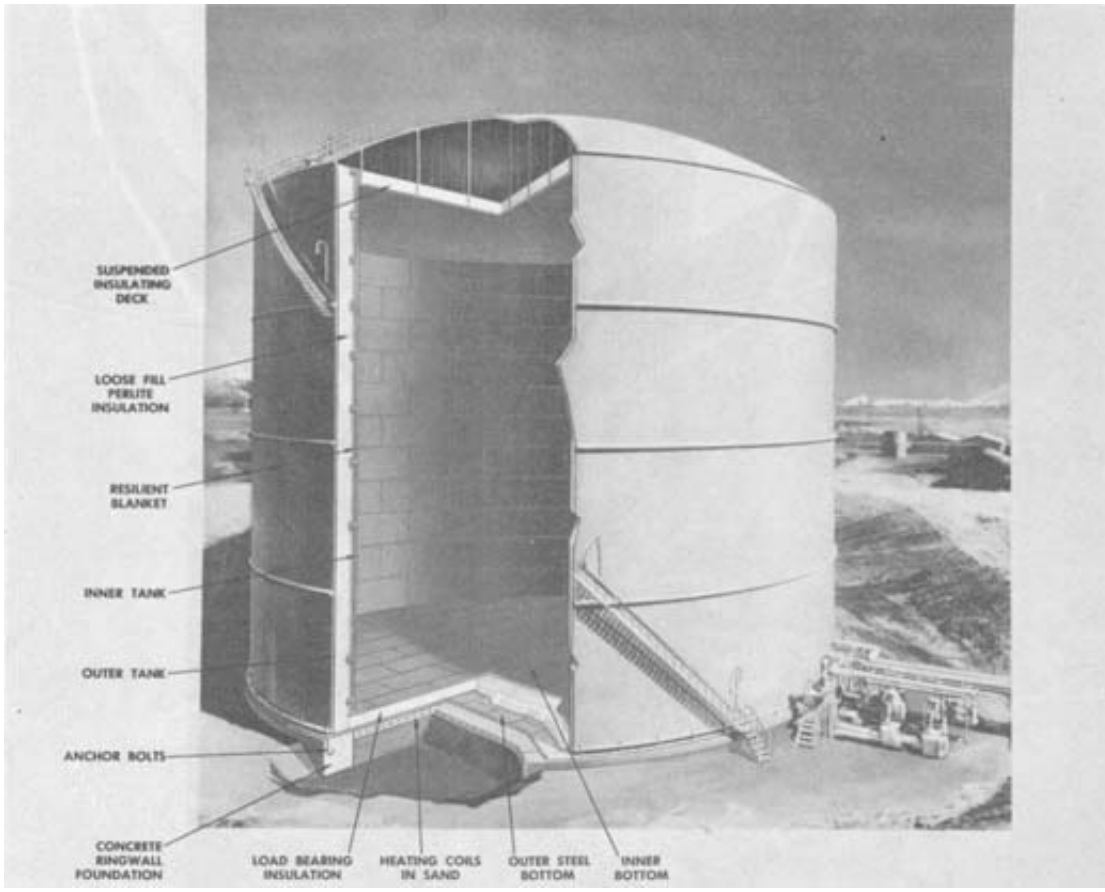


Figure 22.5(b) *Refrigerated atmospheric dome roof double wall tank for LNG (Chicago Bridge and Iron Co.)*

'high-pressure' tanks designed for an internal pressure of 56 mbar and a vacuum of 6 mbar. The maximum design pressure covered by the standard is thus 56 mbar (0.81 psi). BS 2654 also covers floating roof tanks.

Atmospheric tanks are used for the storage of liquids at ambient temperature and also for the storage of refrigerated storage liquids, as described below.

22.3.2 Low pressure storage

Some typical low pressure storage tanks are shown in Figures 22.1(g–i). Figure 22.1(g) shows a horizontal cylindrical tank with dished ends. Figure 22.1(h) shows a vertical cylindrical hemispheroidal tank. Figure 22.1(i) shows a spheroidal tank which has the shape of a squashed sphere. The two latter types are also made in noded as well as plain versions.

Low pressure tanks are designed to withstand internal pressure in the range 0.5–15 psig. The design of low pressure tanks is governed by API Std 620.

Low pressure tanks are suitable for the storage of liquids which are too volatile for atmospheric storage. Gasoline is a typical petroleum product to which this applies. Use is also made of low pressure tanks in refrigerated storage, as described below.

22.3.3 Pressure and refrigerated pressure storage

Some typical pressure storage vessels are shown in Figures 22.1(j) and 22.1(k). Figure 22.1(j) shows a horizontal cylindrical pressure vessel and Figure 22.1(k) a spherical pressure vessel, or Horton sphere.

Pressure storage vessels are regular pressure vessels and can be designed to high pressures as required. The lower end of the scale for pressure storage is 15 psig.

In the USA the design of pressure vessels is governed by the ASME *Boiler and Pressure Vessel Code, Section VIII* (1991) and by API Std 2510: 1989 *Design and Construction of Liquefied Petroleum Gas Installations (LPG)*. The British Standards for pressure vessel design were BS 1500: 1958 and BS 1515: 1965–, which have been superseded by BS 5500: 1991, introduced in 1976. Pressure vessels have been discussed in Chapter 12.

Table 22.3 *Minimum recommended separation distances for the storage of petroleum products: IP* Refining Safety Code *(Institute of Petroleum, 1981 Refining Safety Code)*

	Factor	*Type of tank roof*	*Recommended minimum distance*
(1)	Within a group of small tanks	Fixed or floating	Determined solely by construction/maintenance/ operational convenience
(2)	Between a group of small tanks and another group of small tanks or other larger tanks	Fixed or floating	10 m minimum, otherwise determined by size of the larger tanks (see (3) below).
(3)	Between adjacent individual tanks (other than small tanks)	(a) Fixed	Half the diameter of the larger tank, but not less than 10 m and need not be more than 15 m
		(b) Floating	0.3 times the diameter of the larger tank, but not less than 10 m and need not be more than 15 m[a]
(4)	Between a tank and the top of the inside of the wall of its compound	Fixed or floating	Distance equal to not less than half the height of the tank (Access around the tank at *compound* grade level must be maintained)
(5)	Between any tank in a group of tanks and the inside top of the adjacent *compound* wall	Fixed or floating	Not less than 15 m
(6)	Between a tank and a public boundary fence	Fixed or floating	Not less than 30 m
(7)	Between the top of the inside of the wall of a *tank compound* and a public boundary fence or to any fixed *ignition source*	–	Not less than 15 m
(8)	Between a tank and the *battery limit* of a process plant.	Fixed or floating	Not less than 30 m
(9)	Between the top of the inside of the wall of a *tank compound* and the *battery limit* of a process plant	–	Not less than 15 m

[a] In the case of crude oil tankage this 15 m option does not apply.
Notes: (1) Small tanks are those of up to 10 m diameter; (2) a group of small tanks with a total capacity of 8 000 m^3 may be treated as one tank; (3) where future changes of service are anticipated, the layout should be designed for the most stringent case; (4) in order to allow access for fire fighting, the number of rows of tanks between adjacent access roads should be limited to two; (5) fixed roof tanks with internal floating covers should be treated for spacing purposes as fixed roof tanks; (6) where fixed roof tanks and floating roof tanks are adjacent, the spacing should be designed for the most stringent case; (7) where tanks are erected on compressible soils, the spacing should be such as to avoid excessive distortion; (8) for Class III(1) and Unclassified petroleum liquids, spacing of tanks is governed only by constructional and operational convenience.

Horizontal cylindrical vessels have a relatively limited capacity and for large quantities spheres are used.

Spherical pressure vessels have a number of advantages. The surface to volume ratio is minimal and only 88% of that of a vertical cylindrical tank, which reduces heat leak. The foundation structure is simpler and there is no danger of soil freezing. The stresses under low temperature conditions are easily determined.

Pressure storage vessels are suitable for the storage of liquefied gases such as LPG and ammonia. Pressure storage vessels are also used for refrigerated pressure, or semi-refrigerated, storage.

22.3.4 Refrigerated storage

A typical refrigerated storage tank is shown in Figure 22.1(l). This is a domed roof, flat bottomed tank. It is essentially an atmospheric tank, with a design pressure below 1 psig. Low pressure tanks may also be used for refrigerated storage.

22.3.5 Concrete storage tanks

The need for very large storage capacities for LNG has led to the development of pre-stressed concrete storage tanks which are protected by an earthen embankment, or berm, and are internally insulated.

22.3.6 Underground cavity storage

Underground cavities may also be used for storage. Natural gas has been stored for many years in underground reservoirs, which are frequently depleted oil or gas fields. Use may also be made of such man-made cavities as worked-out salt formations or mined cavities to store gases. The well is usually operated with a brine system, but dry wells are possible also.

22.3.7 Earth pit storage

A method of storing LNG in pits where a hole was excavated and the surrounding earth then frozen was developed and used but the operating problems were such that it has fallen into disuse.

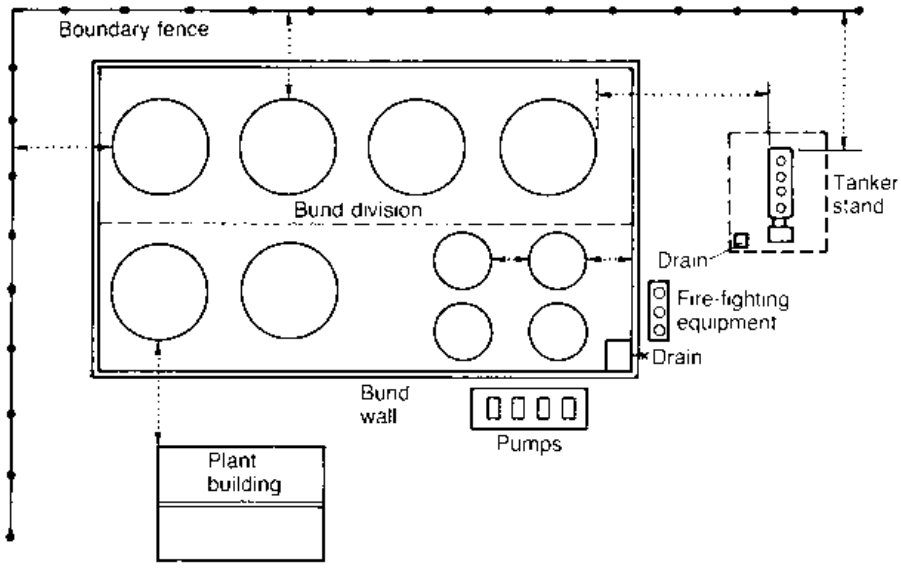


Figure 22.6 *Layout for storage of flammable liquids (Health and Safety Executive, 1991 HS(G) 52) The distances shown by dotted lines should be as in the text and Tables 1 or 2 of HS(G) 52. (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

22.3.8 Gas storage

Gasholders are used to store gases such as hydrogen and acetylene close to atmospheric pressure. Storage of gas under pressure is usually done in gas cylinders or horizontal cylindrical pressure vessels. As already mentioned, gas may also be stored in underground cavities.

22.3.9 Glass reinforced plastic tanks

Widespread use is now made of vessels and tanks made of glass fibre reinforced plastic (GFRP), also known as glass reinforced plastic (GRP), fibre reinforced plastic (FRP) or fibreglass. GRP tanks are widely used to store corrosive materials. They are considered further in Section 22.23.

22.4 Storage Layout

The siting and layout of storage in relation to the process are discussed in Chapter 10. Here the layout within the storage area is considered.

As mentioned in Chapter 10, the storage, process and terminals should be suitably arranged relative to one another, an appropriate layout being one in which the storage is located between the process and the terminals. The storage should be built on ground able to support the heavy load involved and with ground contours and wind characteristics which minimize the hazard of flammable liquid or vapours from storage collected in hollows or flowing across to the process and finding an ignition source.

22.4.1 Segregation

The segregation and separation of materials within the storage area is largely based on classification of the materials stored, on secondary containment, on hazardous area classification and on fire protection measures.

The classification of liquids is described in Chapter 10. Principal classifications are those given in the IP *Refining Safety Code* and in NFPA 30.

Traditionally, the flashpoint classification has been used as a guide to segregation of liquids in storage. Using the earlier classification into classes A, B and C, the main distinction was between Classes A/B and C. This was the basis of the system used in the 1965 version of the IP *Refining Safety Code*. The current code places less emphasis on this type of distinction as far as concerns segregation.

It is convenient to segregate materials which require secondary containment such as bunding, from those which do not. Where the requirements for hazardous area classification are different, it may be convenient to segregate on this basis.

The fire protection which needs to be provided is a fourth means of classification. Fire protection is considered below.

22.4.2 Separation distances

Minimum recommended separation distances for storage are given in various codes and other publications. These were listed in Chapter 10. The separation distances for petroleum products given in the IP *Refining Safety Code* are shown in Table 22.3. The code gives a number of layouts illustrating these separation distances.

Table 22.4 *Minimum recommended separation distances for the storage of flammable liquids: HS(G) 52 (Health and Safety Executive, 1991 HS(G) 52) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

A Fixed roof tanks

Factor	*Minimum separation distance from any part of the tank* (m)
(a) Between groups of small tanks[a] (see note below)	15
(b) Between a group of small tanks and any tank outside the group	15
(c) Between tanks not being part of a group of small tanks	Half the diameter of the larger tank, the diameter of the smaller tank, or 15 m, whichever is least, but never less than 10 m
(d) Between a tank and any filling point, filling shed or building, not containing a possible source of ignition	15
(e) Between a tank and outer boundary of the installation, any designated non-hazardous area, or any fixed source of ignition	15

[a] A group of small tanks, 10 m in diameter or less, may be regarded as one tank. Such small tanks may be placed together in groups, no group having an aggregate capacity of more than 8000 m^3. The distance between individual tanks in the group need be governed only by constructional and operating convenience but should not be less than 2 m.

B Floating roof tanks

Factor	*Minimum separation distance from any part of the tank (*m)
(a) Between two floating roof tanks	10 m for tanks up to and including 45 m diameter; 15 m for tanks over 45 m diameter. The size of the larger tank should govern the spacing
(b) Between a floating roof tank and a fixed roof tank	Half the diameter of the larger tank, the diameter of the smaller tank or 15 m, whichever is least, but never less than 10 m
(c) Between a floating roof tank and any filling point, filling shed or a building not containing a possible source of ignition	10
(d) Between a floating roof tank and outer boundary of the installation, any designated non-hazardous area or any fixed source of ignition	15

C LPG storage[a]

	Distance from flammable liquid tank (m)	*Distance outside bund wall around a flammable liquid tank* (m)
LPG cylinders (>50 kg total capacity)	3(3)	3(0)
LPG vessel	6(6)	6(3)

[a] The figures in brackets relate to liquids with a flashpoint greater than 32°C.

Separation distances for flammable liquids are given in HS(G) 50 and HS(G) 52. Figure 22.6 shows a general layout given in HS(G) 52 and Table 22.4 lists the separation distances given in this guide. These separation distances are for flammable liquids with flashpoints up to 55°C. There are, however, certain relaxations for liquids with a flashpoint in the range 32–55°C, which are described in the guide.

22.4.3 Separation distances: fire models

An alternative approach is to base separation distances on engineering principles. Two main factors which should determine separation are (1) the heat from burning liquid and (2) the ignition of a vapour escape. These principles and their application were discussed in Chapter 10.

The application of such engineering calculations to the separation distances for storage tanks has been treated by Hearfield (1970) and R.B. Robertson (1976b). Calculations on separation distances related to heat effects are usually based on direct flame impingement and on heat radiation.

It is commonly assumed that in a storage tank fire the tank is effectively a pool of liquid with a flame burning

on this liquid and that on a tank of diameter D the height of the flame in still air is $2D$.

If there is a wind, however, the flame is distorted. At a wind speed of 2 m/s it has been observed that the flame is deformed to an angle of 45° to the horizontal and that on the downward side of the fire the flame hugs the ground for a distance of about $0.5D$.

For the heat radiated from the flame it is usually assumed, for simplicity, that still-air conditions prevail. The heat radiated is calculated and compared with limit values.

An equation given by Hearfield and by Robertson for the heat radiated from the envelope of a flame burning on a liquid pool in a storage tank is:

$$Q = k_1 A r \rho C \qquad [22.4.1]$$

where A is the surface area of the pool (m^2), C is the calorific value of the liquid (kJ/kg), Q is the heat radiated from the flame envelope (kW), r the liquid burning rate (m/s), ρ is the density of the liquid (kg/m^3) and k_1 is a constant.

The value of the constant k_1 generally used by these authors is 0.3. Robertson gives liquid burning rates of 0.083–0.17 mm/s (5–10 mm/min). Hearfield gives liquid burning rates of 0.1, 0.3 and 0.4 in./min for 1, 7 and 35 ft diameter pools, respectively.

The application of Equation 22.4.1 is described by Robertson as follows. It is assumed that the heat is radiated from the envelope of a cylinder diameter D and height D, and that in turn this is equivalent to radiation from a radiating area which is a vertical rectangular plane of width D and height $2D$. The heat flux received by another storage tank is obtained from the view factor method. He states that for most hydrocarbon flames the heat radiation from the surface of the cylinder is approximately 170–240 kW/m^2 and suggests that a suitable limit for the heat received by an adjacent storage tank is 37.8 kW/m^2. Other limit values for heat radiation which are relevant to separation were given in Chapter 10.

It is pointed out by Robertson that the separation distances in some storage installations are less than ideal. For example, on many small chemical plants storage tanks approximately 6 m diameter and 6 m high are spaced 2 m apart. If a fire occurs when the wind direction is along the line of the tanks and the wind speed is 2 m/s, the fire would spread rapidly by direct flame impingement. It may not always be possible to have the ideal separation, but the decision on the separation distance should be made with full awareness of the implications. A similar approach may be taken using the more recent models given in Chapter 16.

22.4.4 Secondary containment

Some types of liquid storage tank are normally surrounded by a bund, or dike, and/or provided with a pit to retain any spillage of the liquid, or impounding basin. Bunds are made of earth or concrete.

In general, bunds are provided for atmospheric storage tanks and for fully refrigerated storage tanks of liquefied gas, but not for pressure or semi-refrigerated storage of liquefied gas or for acid or alkali storage, although this generalization needs some qualification.

The object of bunding is to retain the liquid so that it can be dealt with in a controlled manner, by evaporation from a specially designed catchment/evaporation area, by foam blanketing or other measures.

Thus the relatively weak atmospheric storage tanks are generally provided with full bunds, while pressure storage vessels may not be. Bunds tend not to be used for pressure vessels because these rarely fail, the emission when it does occur is mainly in vapour/spray form and the dispersion of small leaks and spillages is hindered. Even where a full bund is not used, however, a low wall may be provided which gives the vessel some protection from damage by vehicles. Low walls may also be used to keep flammable liquids from some external source from reaching a storage vessel.

It may be noted that experience shows that in most cases of tank rupture only a proportion of the liquid in the tank is lost and in many most of the liquid is retained in the tank.

Some practical aspects of the design of bunds for flammable liquids have been discussed by Hearfield (1970). He draws attention to the fact that a leak in the side of a tank may form a horizontal jet and may jump the bund if the latter is too close to the tank, an effect known as spigot flow. The bund wall should be far enough from the side of the tank to prevent a jet jumping over or, alternatively, the bund should be surrounded by an impervious surface sloped inward to the bund drain area. The corners of the bund should be rounded and not at a right angle. It is difficult to extinguish a fire in a 90° angle corner because of the air compression effect.

The IP *Refining Safety Code* gives requirements for tank compounds. It states that Class I, II(1), II(2) and III(2) petroleum liquids should be completely surrounded by a wall or walls. Alternatively the ground should be so sloped that spillages are directed to an impounding basin.

The *Code* gives the following restrictions on the total capacity of tanks in one bunded area: (1) single tanks: no restriction; (2) groups of floating roof tanks, 120 000 m^3 maximum; (3) groups of fixed roof tanks, 60 000 m^3 maximum; and (4) crude tanks, not more than two tanks of greater individual capacity than 60 000 m^3. The figures for (2) and (3) may be exceeded for groups of not more than three tanks where conditions are suitable, i.e. there is no hazard to the public or risk of pollution.

The *Code* states that the net capacity of a tank compound should generally be equivalent to the capacity of the largest tank, but that a capacity of 75% will provide reasonable protection and may be used where conditions are suitable. The net capacity of the compound should be calculated by deducting from the total capacity the volume of all tanks, other than the largest, below the top of the compound wall and the volume of all intermediate walls within the compound.

For Class III(1) and Unclassified petroleum liquids, the code states that a low wall, which need not be more than 0.5 m high, should be constructed around the tankage, where conditions are such that the liquid could escape and cause damage or pollution.

Guidance on bunding for flammable liquids is given in HS(G) 50 and HS(G) 52. In respect of the restrictions on tankage within one bund and of bund capacity the requirements are consistent with, but less detailed than, those of the IP *Code*.

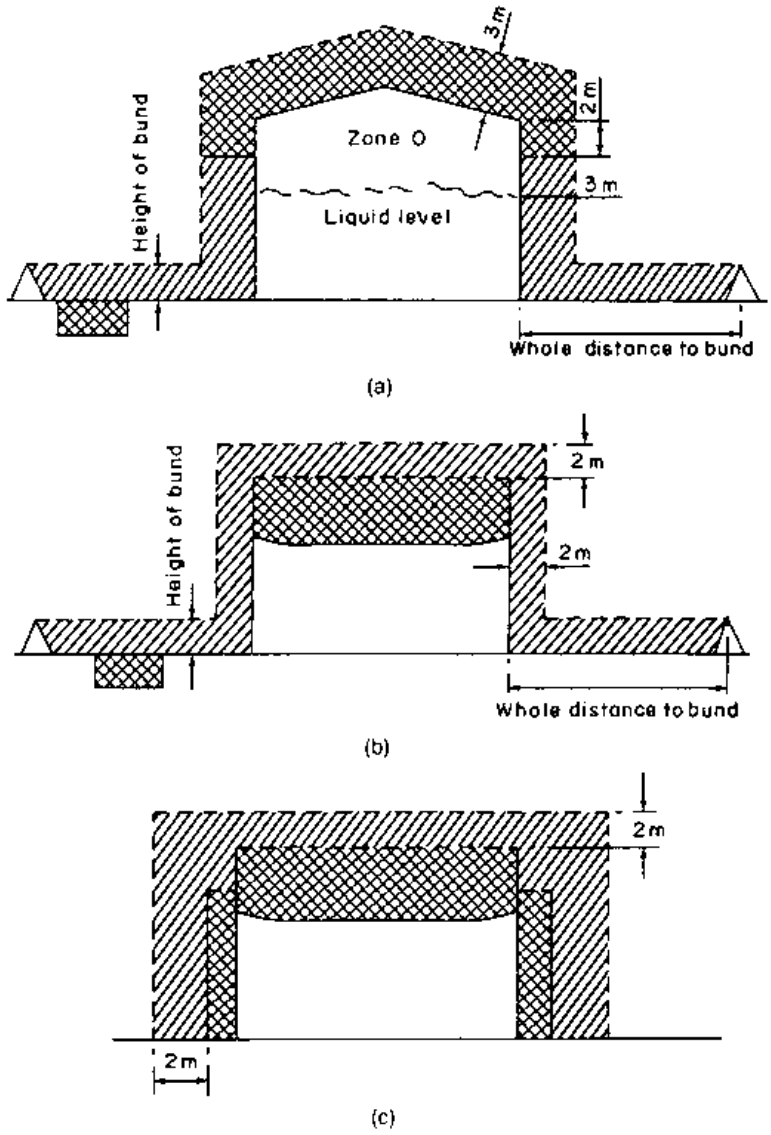


Figure 22.7 *Hazardous area classification of petroleum storage tanks: (a) cone or dome roof tank – Classes I, II(2) and III(2); (b) floating roof tank, where roof will not be grounded on its leg during operational cycle; (c) floating roof tank with outer protective wall; (d) cone roof tank with outer protective wall. for (a), because of the possibility of mist, spray or foam formation the ullage space of Class II(1) and III(1) tanks should also be regarded as Zone 0. It is recommended that the area surrounding any vents or openings on the roof of such a tank be regarded as Zone 1 to a diameter of 1 m. (Institute of Petroleum, 1987 LPG Storage Code; reproduced by permission)*

HS(G) 52 states that the height of the bund wall should be restricted in order to ensure good ventilation, access for fire fighting and means of escape. It should not normally exceed 1.5 m, though it may go up to 2 m provided these factors have been taken into account.

For removal of rainwater, HS(G) 52 requires that where a bund drain is used it should have a valve on the outside of the bund with a system of work to ensure that the valve remains closed, and preferably locked, except when water is being removed. If the liquid stored is immiscible with water, there should be an interceptor to prevent flammable liquid entering the main drainage system. If the liquid is miscible with water, special arrangements are needed.

Guidance on bunds is also given in NFPA 30 and BS 5908. A further discussion of bunding is given in Section 22.21.

22.4.5 Hazardous area classification

Control of ignition sources in storage areas is exercised through the system of hazardous area classification

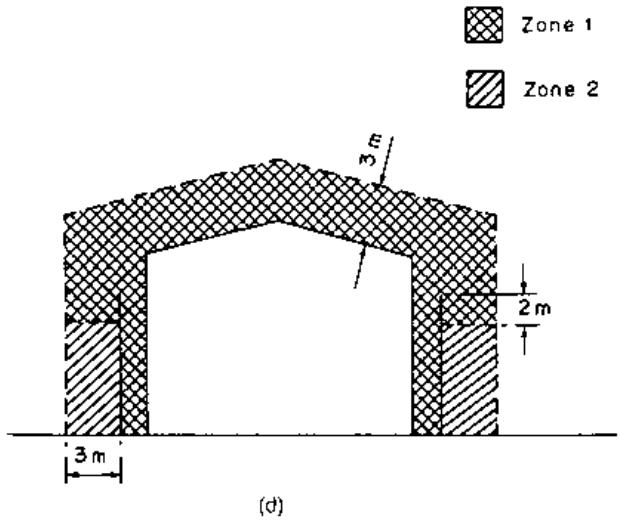


Figure 22.7 *continued*

(HAC). The principles of HAC have been described in Chapters 10 and 16.

Guidance on HAC for refineries, including storage, is given in API RP 500: 1991 *Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Facilities*. This supersedes the separates RPs 500A, 500B and 500C, which covered refineries, offshore rigs and platforms, and pipelines, respectively. Guidance on HAC for storage is given in the *Area Classification Code for Petroleum Installations* of the IP (1990 MCSP Pt 15) (the IP *Area Classification Code*). The guidance of the Health and Safety Executive (HSE) is given in HS(G) 50 and HS(G) 52.

Figure 22.7 shows some HAC classification diagrams for petroleum storage tanks given in the IP *Area Classification Code*. Table 22.5 from HS(G) 52 gives some principles for the delineation of the zones around storage tanks in the HAC.

22.5 Venting and Relief

22.5.1 Atmospheric vents

A fixed roof atmospheric storage tank is connected to the atmosphere by some form of a vent, generally either a simple free flow atmospheric vent or a pressure/vacuum valve.

Vents for atmospheric storage tanks are dealt with in BS 2654: 1989 in Appendix F and in API Std 2000: 1992 *Venting Atmospheric and Low Pressure Storage Tanks (Non-refrigerated and Refrigerated)*.

Since atmospheric tanks can withstand pressure/vacuum of only a few inches WG, it is essential that atmospheric vents should remain free. Blockage can occur accidentally due to debris, icing up, solids formation, polymerization, etc.

A flame arrester on the end of a vent also serves to keep out debris. If there is no arrester, a coarse wire mesh guard is usually provided. But there is a danger of blockage of flame arresters and guards. The use of flame arresters is considered further below.

The tank may also suffer overpressure or underpressure if the capacity of the vent is not sufficient. Pressure changes occur mainly during filling and emptying, but also in other circumstances.

Situations in which tank failures tend to occur due to accidental blockage or deliberate sealing off of a vent, or to lack of capacity in the vent, were described in Chapter 20.

22.5.2 Pressure/vacuum valves

A pressure/vacuum (PV) valve, also called a breather valve or conservation vent, actually has two vent valves – a pressure valve which opens to let vapour out and a vacuum valve which opens to let air in.

A fixed roof tank tends to breathe fairly heavily and appreciable vapour loss can occur through an atmospheric vent, particularly for a volatile liquid. A PV valve is effective in reducing this loss.

Avoidance of blockage and provision of adequate capacity are important for PV valves also. PV valves are subject to failure from icing up and deposition of material on the valve diaphragms or in the branch on the tank. The danger of ice formation is usually most severe just after the tank has been water tested, and the valve diaphragms are often removed for about 2 weeks until the water content of the liquid has reduced to normal, although the problem is less with newer diaphragm materials such as PTFE.

22.5.3 Flame arresters

If the vapour space above the liquid in a fixed roof atmospheric storage tank contains a flammable mixture, there is a possibility that it will be ignited via the vent. A flame arrester may be used to prevent this.

Table 22.5 *Guidelines for the hazardous area classification of the storage of flammable liquids (Health and Safety Executive, 1991 HS(G) 52) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

Item	*Extent of area*	*Classification*
Above-ground tanks	(a) Vertically from ground level to the height of the bund wall, and horizontally from the tank shell to 1 m outside the bund wall	Zone 2
	(b) Within 2 m of the tank shell	Zone 2
Underground tanks	Within any manhole chamber containing filling connections	Zone 0
Tank connections (all tanks)	Within a horizontal radius of 4 m from tank filling connections, and vertically from ground level up to 1 m above the connections	Zone 2
All tanks	Within the vapour space	Zone 0
Vent pipes	(a) Within a radius of 3 m in all directions of the open end of any vent pipe	Zone 1
	(b) The area below the Zone 1 area of any vent pipe, for a radius of 3 m around the discharge point and down to ground level	Zone 2
Pumps and sample points	Within a horizontal radius of 4 m and vertically from ground level to 2 m above the unit	Zone 2
Road and rail tankers (at loading/unloading points)	(a) Withn 300 mm in any direction of any opening on the tanker, and down to ground level	Zone 1
	(b) Within 2 m of the shell of the tanker	Zone 2
	(c) Within a horizontal radius of 4 m from tanker discharge connections and vertically from ground level up to 1 m above the connections	Zone 2
	(d) Within a radius of 1.5 m of any opening on the tank top, and down to ground level	Zone 1
	(e) On the top of the tank within the valence	Zone 1

Notes:
(1) Where an area is classified under more than one heading the more stringent classification should be adopted.
(2) Any pit, trench or depression in a Zone 1 or Zone 2 area should be considered a Zone 1 area throughout.
(3) Where tanks are mounded or buried in a hillside, etc., and access is by means of a tunnel or adit, typically 2 m or more in height, the space in the tunnel should normally be considered a Zone 1 area.

Flame arresters have already been discussed in Chapter 17. General accounts are given in *Guide to the Use of Flame Arresters and Explosion Relief* by the HSE (1965 HSW Bklt 34) and API Publ. 2028: 1991 *Flame Arresters in Piping Systems*. The discussion here is limited to the question of their use on storage tank vents.

The object of a flame arrester is to prevent a flame passing back through a vent to ignite a flammable mixture in the vapour space of the tank. Consideration needs to be given, therefore, to the conditions under which a flammable mixture can exist. The range of materials stored is such that for some the vapour mixture is below the lower flammability limit, while for others it is above the upper flammability limit, but for others again it is in the flammable range. The situation is also affected by the use of a floating deck. This reduces the concentration of vapour, but does not necessarily eliminate flammable mixtures. The vapour space above the floating deck may in fact go from a mixture above the upper flammability limit near the deck to one below the lower flammability limit near the fixed roof.

It is also necessary to consider the conditions under which a flame can occur at the vent outlet. For this to happen the vent must be exhaling vapour. It may be assumed that it does this, on average, half the time. The situations which give rise to exhalation of vapour are, in particular, filling operations and temperature rises. Thus the conditions under which a flame may flash back and cause an explosion are when the vapour space in the tank contains an explosive mixture and the vent is exhaling vapour.

The desirability of using flame arresters has been a matter of some debate. Insurance companies have often recommended their use. Thus the Factory Mutual Engineering Corporation (FMEC, 1967) recommends their use on atmospheric vents for liquids with flash points below 110°F (43°C) and for liquids which may be heated above their flashpoints.

A discussion of the problem is given in API Publ. 2210: 1982 *Flame Arresters for Vents of Tanks Storing Petroleum Products*, though this is no longer listed. Flame arresters are a potential cause of vent blockage and tank collapse and their use needs to be justified.

The case for the use of a flame arrester in addition to a PV valve is less than clear. API Publ. 2210 suggests that where a PV valve is used, there is no good reason to put a flame arrester on.

The argument supporting this view is broadly on the following lines. Tank fires caused by lightning were a problem on the older wooden-roofed tanks, but with the advent in about 1920 of truly gas-tight steel roofs combined with PV valve such fires are rare. The probability of tank fires via vents is low, because most oil industry stocks do not give a vapour mixture in the flammable range above the liquid, and ignition sources are excluded from the vicinity of vents. Moreover, it is

notoriously difficult to keep flame arresters well maintained and this introduces the hazard of vent blockage and tank collapse.

API Publ. 2210 concludes: 'There is no supportable basis for requiring that an outdoor above-ground tank provided with a pressure–vacuum valve must also be equipped with a flame arrester. The use of flame arresters is discouraged unless the user is able to institute the maintenance necessary to ensure that the required venting capacity is maintained.'

API Std 2000: 1992 takes a similar stance, stating: 'A flame arrester is not considered necessary for use in conjunction with a PV valve because flame speeds are less than vent velocities through PV valves'. It does, however, go on to say: 'Open vents with a flame-arresting device may be used in place of PV valves on tanks in which oil with a flash point below 100°F (37.78°C) is stored and on tanks containing petroleum and petroleum products where the fluid temperature may exceed the flash point'.

The IP *Refining Safety Code* states that fixed roof tanks for Class I and II liquids are usually fitted with PV valves and tanks for Class III and Unclassified liquids with open vents. It further states that PV valves or open vents should not be fitted with fine mesh gauze, which is liable to clog.

HS(G) 50 and H(G) 52 state that a flame arrester should normally be installed on an open vent on a fixed roof tank storing liquid with a flash point below 21°C. But a flame arrester is not necessary on a PV valve and should not be used where the liquid is liable to block the arrester by polymerization or otherwise.

22.5.4 Fire relief

It is also necessary for fixed roof storage tanks to provide for the effect of fire which heats the liquid, increases its vaporization and causes a rise in pressure. Tanks can normally withstand a pressure of only a few inches WG. It is normal not to size atmospheric vents or PV valves for fire relief but to provide for this by separate emergency venting.

Methods of providing emergency venting for fire are described in API 2210. They include larger or additional open vents, larger or additional PV valves, lifting manhole covers or hatches, and a weak roof-to-shell connection.

This latter arrangement involves the use of a weak roof-to-shell attachment, otherwise known as a frangible joint or rupture seam. This involves making the seam between the shell and the roof deliberately weak so that it is the first to rupture, thus ensuring that the shell stays intact and contains the liquid. The incorporation of such a frangible joint as an emergency vent in accordance with API 2210 is allowed for in API Std 650. Not all companies consider it good practice to rely on a rupture seam for fire relief, although one may still be used to relieve explosions.

The methods given in API Std 2000 for the determination of the heat input into storage tanks in a fire, and hence of the venting capacity required, are described in Chapter 16.

22.6 Fire Prevention and Protection

Accounts of fire prevention and protection of petroleum storage are given in *Storage and Handling of Petroleum Liquids* by J.R. Hughes (1970) and *Fire Protection Manual for Hydrocarbon Processing Plants* by Vervalin (1964a, 1973a). Relevant standards and codes are API RP 2001: 1984 *Fire Protection in Refineries*, the IP *Refining Safety Code*, NPFA 30: 1990 *Flammable and Combustible Liquids Code*, BS 5306: 1976– *Fire Extinguishing Installations and Equipment on Premises* and BS 5908: 1990 *Code of Practice for Fire Precautions in the Chemical and Allied Industries*. HSE guidance is given in HS(G) 50 and HS(G) 52.

Fire prevention in and protection of storage has several objectives. These are (1) to minimize the risk to personnel, (2) to minimize loss due to the initial fire, and (3) to prevent the spread of fire to other vessels and equipment. Personnel are at risk principally from an explosion or sudden spread of fire.

Implementation of fire protection for storage takes the two forms (1) fighting the fire and (2) protecting the storage vessels. Methods of fire prevention and protection in general have been described in Chapter 16. The discussion there includes some treatment of storage, including the application rates of fire fighting media.

A major contribution to fire prevention in storage is made by layout, as described in Section 22.4. Important aspects of storage layout are the practice of segregation, the provision of separation distances and hazardous area classification.

22.6.1 Inerting of storage tanks

An effective method of fire prevention in storage is inerting. This is widely used to reduce the hazard of fire in atmospheric storage tanks. The value of inerting in reducing fire/explosion in storage tanks was discussed in Chapter 16 and methods of inerting were described in Chapter 17.

22.6.2 Fire protection of storage tanks

There are two main effects of fire on an atmospheric storage tank. One is that those parts of the tank which are not cooled by the liquid inside may become hot and weaken. The other is that the liquid inside the tank is heated up and its vaporization is increased. In a fixed roof storage tank this results in a pressure rise and, as explained earlier, relief of such pressure is now normally effected by the use of some form of emergency vent.

Fire protection for atmospheric storage tanks is provided by fixed water or foam sprays, which may be supplemented by fireproof thermal insulation, and by mobile water and foam sprays.

Fixed water sprays are effective in giving immediate cooling of exposed surfaces and are particularly useful where manpower is limited or access for mobile equipment is difficult. But the main water sprays are normally provided by mobile equipment and are used both to fight the fire and to cool exposed surfaces. There are also mobile water curtains which can be interposed to protect vessels if sufficient manpower is available.

For cooling of an unwetted tank surface a rate of application of water of 0.2 UKgal/ft^2 min (10 l/m^2 min) has been found satisfactory. It is desirable to cool the wetted surface also to minimize the rise in pressure, but

the effectiveness of water cooling then depends on the boiling point of the stored liquid. If this is below the boiling point of water, the water does not vaporize and the cooling due to the latent heat effect is not obtained. If, however, the boiling point of the liquid is above that of water, then the water does vaporize and is much more effective.

Foam is used to extinguish fires rather than to cool surfaces. The type of foam used is normally mechanical foam. Fixed foam pourers are used to direct foam to the inside of the tank shell so that the foam flows over the liquid surface. Another fixed device which puts foam on the liquid surface is the Swedish semi-subsurface foam system. This consists of a hose which is connected through the tank shell to a foam supply and is normally at the bottom of the tank. Injection of foam inflates the hose, the top end of which rises to the liquid surface and sprays the foam.

Mobile foam-spraying equipment consists of mobile monitors and portable foam towers. A monitor projects jets of foam in a manner similar to that of conventional fire water jets. A portable tower is a light tube which is put up the side of the tank and pours foam on the top of the liquid. There are various types, some assembled manually and others of telescopic design extended mechanically or hydraulically.

Mobile foam monitors are available with a foam output of 5000 UKgal/min and a range of 60 m (200 ft) in still air. For extinguishing fire a rate of application of foam of 0.1 UKgal/ft^2 min (4.5 l/m^2 min) has been found necessary.

Fixed equipment such as foam pourers is very vulnerable to damage by explosion.

The application of foam from foam monitors requires some skill. An experienced operator can project foam so that it hits the inside of the tank on fire and runs down and blankets the burning liquid.

The amount of foam used is large and it is necessary to make arrangements for adequate supplies.

22.6.3 Pipework and fittings

Fire can also have a very damaging effect on pipework, which sometimes may withstand the fire for only about 10 minutes. Pipework is very vulnerable to fire and should be protected as far as possible. Fireproof insulation on pipework near storage vessels may be appropriate.

A small fire at a leaking flange can have a torch effect and this possibility should be borne in mind in designing pipework. A fire of this type was one of the causes considered at the Flixborough Inquiry.

22.7 LPG Storage

Some aspects of the storage of other fuels and chemicals are now considered, starting with liquefied petroleum gas (LPG). The handling and processing of many of these substances were treated in Chapter 11 and the design of pressure systems in Chapter 12, and these topics are therefore not discussed here. However, attention is drawn to the fact that aspects such as the materials of construction, the pipework, the valves and the pumps are particularly important for these chemicals.

Propane and butane are referred to as liquefied petroleum gas (LPG). They are described in *An Introduction to Liquefied Petroleum Gas* (LPGITA, 1974/1). A general account of LPG is given in Chapter 11.

Codes and standards for LPG were given in Chapters 10 and 11. HSE guidance on LPG storage is given in HS(G) 34 *The Storage of LPG at Fixed Installations* (1987). Other relevant codes are *Design, Installation and Maintenance of Bulk LPG Storage at Fixed Installations* (LPGITA, 1991 COP 1 Part 1) (the LPGA *LPG Storage Code*), NFPA 58: 1989 *Storage and Handling of Liquefied Petroleum Gases* (also published as the *Liquefied Petroleum Gases Handbook*) and NFPA 59: 1989 *Storage and Handling of Liquefied Petroleum Gases at Utility Plants*. The code *Liquefied Flammable Gases Storage and Handling* (ICI/RoSPA 1970 IS/74) (the ICI *LFG Code*), though out of print, contains much valuable guidance.

LPG is stored at petroleum storage terminals, at chemical works and at many non-chemical factories.

22.7.1 Regulatory requirements

The storage of LPG is governed by the Notification of Installations Handling Hazardous Substances (NIHHS) Regulations 1982 and the Control of Industrial Major Accident Hazards (CIMAH) Regulations 1984. The NIHHS notifiable inventory is 25 te for pressure storage and 50 te for refrigerated storage. The CIMAH inventory for either type of storage for which demonstration of safe operation may be required (Regulation 4) is 50 te and that which attracts a safety case (Regulation 7) is 200 te.

An account of the regulatory requirements for LPG in Germany has been given by Ackermann (1986).

22.7.2 Storage conditions

Fully refrigerated storage is essentially at atmospheric pressure and at the boiling points of the substances concerned. For pressure storage the temperature follows the ambient temperature and the pressure is the corresponding vapour pressure of the substance. The boiling point of pure propane is -42°C and that of pure *n*-butane is 0°C. The boiling point of commercial propane is -45°C and that of commercial butane is -2°C. At a pressure reference temperature of 38°C the vapour pressure exerted by commercial propane is 4.83 barg and that exerted by commercial butane is 14.5 barg.

22.8 LPG Storage: Pressure Storage

22.8.1 Storage vessels

Pressure storage of LPG is in horizontal cylindrical or spherical pressure vessels. The former are used for smaller quantities and the latter for larger ones.

The design of pressure vessels for LPG pressure storage is discussed in the Liquefied Petroleum Gas Association (LPGA) *LPG Storage Code*. The design pressures and temperatures should take into account the extreme ambient and service conditions to which the storage may be subject. The *Code* states that the design conditions should not be less onerous than the following:

	Commercial butane	*Commercial propane*	
		Liquid offtake	*Vapour offtake*
Maximum temperature (°C)	38	38	38
Maximum pressure (barg)	4.83	14.5	14.5
Minimum temperature (°C)	−18	−18	−40
Minimum pressure (mbarg)	−524	Zero gauge	Zero gauge

The values given for the maximum temperature, or pressure reference temperature, are for a vessel finished in white; a higher maximum design temperature and pressure should be used for a vessel in a finish which reduces normal reflection of solar radiation. A higher minimum temperature should be used only for dedicated service where controls are provided to limit the lowest fluid temperature to a value higher than that shown. A higher minimum pressure for butane should be used only if means are provided to ensure that an unacceptable vacuum does not occur or if the ambient temperature is such as to ensure that the fluid temperature will be higher than −18°C.

As the LPGA *Code* indicates, more stringent design pressures and temperatures may be appropriate. Some of the factors which bear on this are discussed in the ICI *LFG Code*. For the maximum reference temperature in the UK the *Code* suggests that the following temperatures be assumed for a hot summer day:

Temperature (°C)	*Tank capacity* (m^3)
47.5	< 5
42.5	5–30
41	30–100
40	>100

The *Code* states that the design pressure at the top of the vessel should be set equal to the greater of (1) 110% of the maximum operating pressure or (2) the maximum operating pressure plus 1 bar (14.5 psi), and that the design pressure at the bottom of the vessel should be set equal to that at the top plus the static head of the product or water, whichever is the greater.

The choice of design pressure should also be considered in conjunction with relief and blowdown arrangements, since these can be expensive, and it may be economic to increase further the design pressure.

The maximum design temperature for pressure storage vessels is determined by the loss of strength in the metal at high temperatures. Increased temperature always leads to loss of strength, but the fall-off is much greater for a vessel designed to an advanced code rather than a conventional one. The ICI code states, for example, that the design stress for a vessel designed to BS 1500 does not reduce significantly until 400°C, whereas that for a vessel designed to BS 1515 falls off rapidly above 50°C, so that the maximum design temperature needs to be considered particularly carefully when using BS 1515. The maximum temperature reached by the metal is likely to be during a fire. The temperature of unprotected metal rises rapidly in a fire, but there are several features which may mitigate this. The metal is normally protected by fire insulation and water sprays, and metal in contact with the liquid inside is cooled by the liquid boil off.

The minimum design temperature for pressure storage vessels is normally set by the loss of ductility and hence brittle fracture in the metal at low temperatures. There are several ways in which a low metal temperature may occur. The ambient temperature may be low, although in this case there is normally a time lag due to insulation. The metal may come in contact with low temperature liquid due to abnormal operating conditions in the process or loss of pressure and liquid boil off in the vessel. This latter effect, however, is likely to signal its presence and the *Code* suggests that it may be assumed that for a vessel of reasonable size action would be taken before the temperature has fallen to that corresponding to atmospheric pressure.

The combinations of pressure and temperature which may occur should also be considered.

The material of construction of most storage vessels is carbon steel, but other materials may be used.

A classic set of general arrangements for pressure storage vessels is given in the ICI *LFG Code*. Figure 22.8(a) shows those for a horizontal cylindrical vessel and Figure 22.8(b) shows those for a spherical vessel. Another set of general arrangements for such vessels given by Nazario (1988). Figure 22.9 shows the arrangements for horizontal cylindrical storage vessels given in HS(G) 34.

22.8.2 Separation distances

Separation distances for pressurized LPG storage are given in HS(G) 34, the IP *LPG Code* and NFPA 58.

Minimum separation distances for LPG pressure storage vessels given in HS(G) 34 are shown in Table 22.6. Guidance is also given on separation distances between LPG and storages of flammable liquids, toxic substances, LPG cylinders and cylinder filling buildings. For flammable liquids the separation distance is 6 m to the bund wall for liquids with a flashpoint < 32°C or 6 m to the tank and 3 m to the bund wall for liquids with a flashpoint of 32–65°C. For toxic or hazardous substances the separation distance is as given in Table 22.6 for buildings, etc., subject to a minimum value of 15 m. HS(G) 34 also gives the separation distances between LPG and liquid oxygen storages.

The approach to minimum separation distances in NFPA 58 is broadly similar. This code also gives separation distances between LPG and both oxygen and hydrogen storages.

The approach to minimum separation distances in Germany is described by Ackerman (1986).

22.8.3 Separation distances: fire models

As described earlier, an alternative approach to the setting of minimum separation distances is the use of

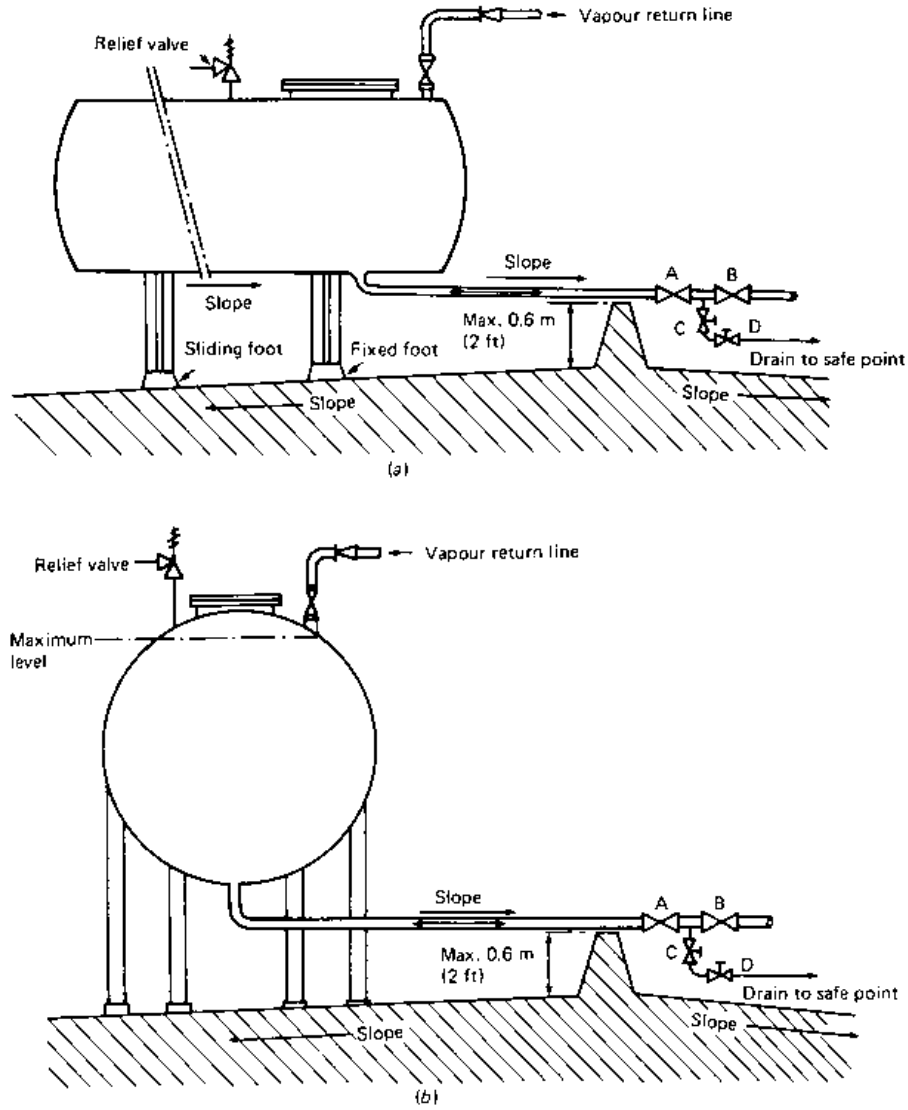


Figure 22.8 *General arrangement of LPG pressure storage vessels with special reference to piping: (ICI/RoSPA 1970 IS/74; reproduced by permission): (a) horizontal cylindrical vessel; (b) spherical vessel*

models for vapour dispersion and fire radiation. An account of the application of this approach to petroleum storage is given in Section 22.4.

The separation distances for LFG given in the ICI *LFG Code*, and shown in Table 22.7, owe something to this approach, and are an early, if implicit, example of its use. Two methods of determining the heat received by pressure vessels are also presented in this *Code*, but these are not used there to determine separation distances, which are obtained from Table 22.7. The two methods are used to calculate the requirements for pressure relief and for drench water as described below.

The modelling approach to separation distances is now entering mainstream codes. The minimum separation distances given in the IP *LPG Code* for LPG pressure storage are specified in terms of the thermal radiation flux from certain defined fires. These fires are jet fires from the vessel relief valve and spillages from the vessel, its associated equipment and other identified leak sources, with spillage possibly forming a pool in the

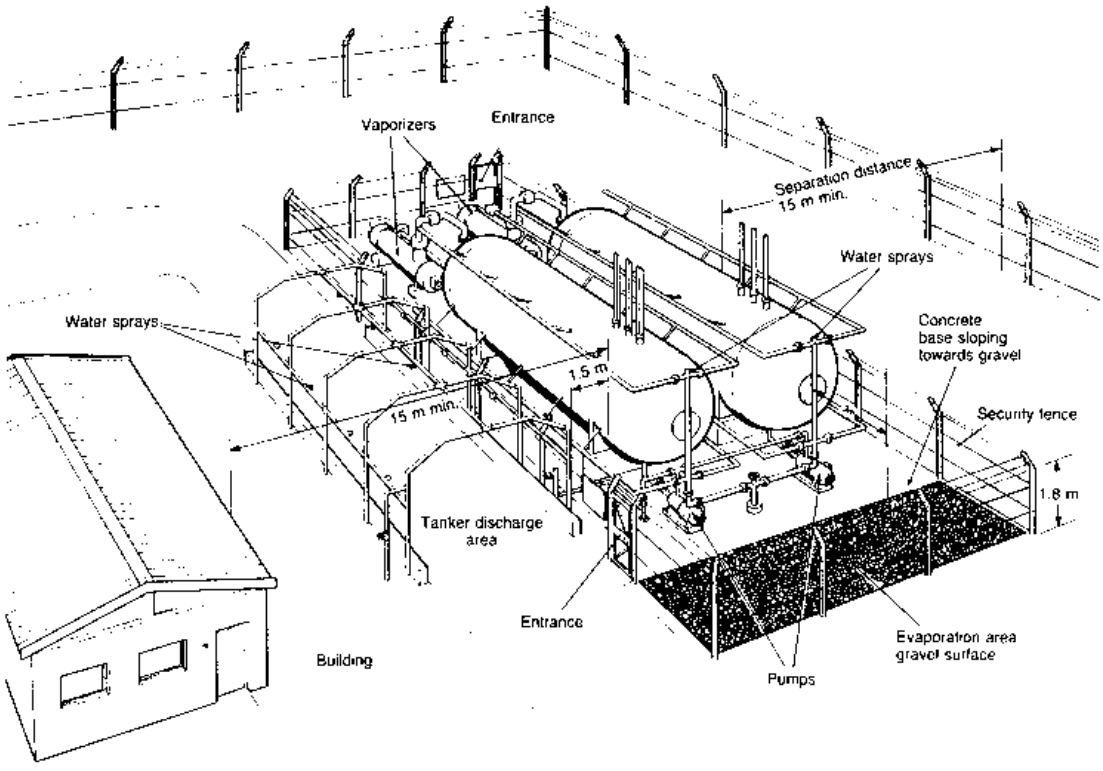


Figure 22.9 *General arrangement of LPG horizontal pressure storage vessels (Health and Safety Executive, 1987 HS(G) 34) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

bund or impounding basin. The *Code* gives guidance on potential leak sources and emission rates and on the thermal radiation from jet and pool fires. The minimum separation distances given in the code are shown in Table 22.8.

22.8.4 Secondary containment

For pressure storage vessels containing LFG a full bund is not used. It is true that an appreciable proportion of a spillage remains as liquid after the initial flashing off of vapour. For example, if liquid propane at 16°C escapes to atmosphere the theoretical proportion of liquid remaining after flashing off is 67%.

However, complete loss of containment from a properly designed, maintained and operated pressure vessel is rare, material is in any case ejected mainly as vapour/spray, and smaller spillages from valvework can be dealt with by other means. Moreover, it is essential to allow free circulation of air so that small leaks and spillages are safely dispersed.

The arrangement recommended in the ICI *LFG Code* is that there should be a diversion wall with only the vessel on one side and all the joints and valvework on the other. The only requirement on the vessel side of the wall, where the risk of spillage is remote, is that the ground should slope away from the vessel, but on the other side there should be not only sloped ground and a catchment area but such diversion walls as are necessary to ensure that a spillage flows into the latter. In an existing installation or other installation in which it is not possible to eliminate joints and valvework under the vessel, these diversion walls should be put around the vessel.

The vessel and its pipework should also be protected against damage by vehicles, by the use of some form of crash barrier if necessary.

HS(G) 32 adopts a broadly similar approach, based on the principles of sloping the area under pipework connections, the use of diversion walls and an evaporating area, and the provision of a crash barrier against vehicle impact. It requires that the ground be impervious beneath the pipework connections, that the height of diversion walls should not exceed 0.5 m and that the evaporation area should be not less than 3 m from the vessel.

The IP *LPG Code* explicitly states that a bund is not normally required and its provisions are in line with the approaches just described.

The ICI *LFG Code* also considers pressure storage of non-hydrocarbon LFGs which are miscible with water and which it may be desirable to dilute. Thus, if the liquid can be rapidly diluted with water and rendered harmless, this is appropriate, and it is then not necessary to provide a catchment area for spillage. But some

Table 22.6 *Minimum recommended separation distances for LPG pressure storage: HS(G) 34 (Health and Safety Executive, 1987 HS(G) 34) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

Vessel capacity (te)		*Distance* (m)[a]		
Single vessel	*All vessels in a group*	*From buildings, boundary, property line or fixed source of ignition*	*With fire wall*	*Between vessels*
4–60	200	15	7.5	1.5
60–150	450	22.5	11	–[b]
>150	1000	30	15	–[b]

[a] These distances apply to above ground vessels. For mounded vessels the distances are as follows. The distances between buildings, etc., and the valve assembly are the same as those for above ground vessels with a fire wall; the distances between buildings, etc., and the vessel itself are 3 m in each case. The distances between vessels are 1.5 m for the lowest set of capacities quoted, but for the two higher sets the spacing should be determined by the site conditions and the requirements of installation, testing, maintenance and removal.
[b] One-quarter of the sum of the diameters of two adjacent vessels.

materials may need to be diluted for other reasons, e.g. toxicity. In this case a full bund should be provided sufficient to take both the spillage and the dilution water. Walls should not exceed 2 m (6 ft 6 in.) in height and they should have at least two access points.

22.8.5 Diversion walls and fire walls

Diversion walls can be used to divert large vapour flows to areas where they can be dealt with more safely.

Steam curtains may also be considered as a means of maintaining separation from an ignition source, although they are actually used mainly around process plants.

Fire walls are utilized to give protection against flame or heat radiated from a fire.

Trenches leading from the storage area should be fire stopped at or near the boundary by barrier walls or bunds across the pipes. Drains with openings in the storage area should have means to prevent the transmission of insoluble flammable and noxious products to the general drainage system.

22.8.6 Hazardous area classification

Guidance on the hazardous area classification (HAC) for LPG pressure storage is given in API RP 500, the IP *Area Classification Code*, and also in NFPA 58 and 59, the LPGA *LPG Storage Code* and HS(G) 34.

A table of guidelines for delineation of the zones round LPG pressure storage vessels for HAC is given in the LPGA *LPG Storage Code*. The virtually identical table given in HS(G) 34 is shown in Table 22.9.

For LPG storage during distribution the IP *Area Classification Code* refers to the LPGA *Code*, whilst for storage under the more varied conditions which pertain in refineries and process plants it advises the use of the point source method.

22.8.7 Pipework and fittings

The pipework, valves and other fittings for storage systems should be designed in accordance with approved practice for such equipment. Pipework for pressure systems was described in Chapter 12 and the discussion here is limited to aspects particularly relevant to storage.

Pipework and fittings for LPG pressure storage are dealt with in the main LPG codes mentioned and also specifically in *LPG Piping System Design and Installation* (LPGA, 1990 COP 22) (the LPGA *Piping Systems Code*).

The types of consideration which should be taken into account in pipework for storage are illustrated by the following recommendations for pipework for LFG taken from the ICI *LFG Code*.

The minimum temperatures which may be attained by the piping should be carefully considered and materials of construction selected accordingly. Storage systems are subject to such operational conditions as rapid blowdown, which can result in low temperatures.

Allowance should be made in the pipework for stresses due to movement, expansion/contraction and vibration. In storage systems typical causes of stress are shifting and settling of vessels and expansion/contraction due to temperature changes.

Joints should be welded or flanged. Welded joints are preferable and flanged joints should be kept to a minimum.

Valves should be of the wedge gate or ball type. Ball valves give a more positive shut-off than wedge gate valves and should be used on the critical filling/discharge and drain lines.

The ball valves should be dual directional, should be of the fire-safety type and should have antistatic protection. Ball valves welded into lines should be such that they can be maintained *in situ* by 'top entry'.

With a ball valve, liquid can be trapped in the body cavity. In low temperature LFG duties conditions can occur which cause the liquid to expand. Provision should be made for relieving this expansion which does not render the valve unidirectional.

The main filling/discharge line should have a minimum diameter of 4 in. The drain line should be 2 in., reducing to $\frac{3}{4}$ in.

The preferred pipework arrangement for a horizontal storage vessel is shown in Figure 22.8(a). There are no flanges, valves or other fittings on the filling/discharge line on the vessel side of the separation wall, only a single butt weld. Valves A–C are butt-welded ball valves and valve D is a flanged, spring-loaded valve. Valve A is

Table 22.7 *Minimum recommended separation distances for LFG storage: ICI* LFG Code *(ICI/RoSPA, 1970; reproduced by permission)*

Minimum distance	*Material stored*					
	Hydrocarbons		*Non-hydrocarbons insoluble in water*		*Non-hydrocarbons soluble in water*	
Pressure storage[1]						
To boundary, process units, buildings containing a source of ignition, or any other fixed sources of ignition	Ethylene C_3s C_4s	60 m (200 ft) 45 m (150 ft) 30 m (100 ft)	Methyl chloride Vinyl chloride Methyl vinyl ether Ethyl chloride	23 m (75 ft) 23 m (75 ft) 23 m (75 ft) 15 m (50 ft)	Methylamines	15 m (50 ft)
To building containing flammable materials, eg. filling shed.		15 m (50 ft)		15 m (50 ft)		15 m (50 ft)
To road or rail tank wagon filling points		15 m (50 ft)		15 m (50 ft)		15 m (50 ft)
To overhead power lines and pipebridges		15 m (50 ft)		15 m (50 ft)		15 m (50 ft)
To other above ground power cables and important pipelines or pipelines likely to increase the hazard	(2)	7.5 m (25 ft)	(2)	7.5 m (25 ft)	See Note (3)	
Between pressure storage vessels	One-quarter of sum of diameters of adjacent tanks					
To low pressure refrigerated tanks	15 m (50 ft) from the bund wall of the low pressure tank, but not less than 30 m (100 ft) from the low pressure tank shell					
To flammable liquid[4] storage tanks	15 m (50 ft) from the bund wall of the flammable liquid tank					
Low pressure refrigerated storage[5]						
To boundary, process units, buildings containing a source of ignition, or any other fixed sources of ignition[6]	Ethylene 90 m (300 ft) C_3s C_4s	45 m (150 ft) 15 m (50 ft)			Ethylene oxide	15 m (50 ft)
To building containing flammable materials, e.g. filling shed		15 m (50 ft)				15 m (50 ft)
To road or rail tanker filling point		15 m (50 ft)				15 m (50 ft)
To overhead power lines and pipebridges		15 m (50 ft)				15 m (50 ft)
Between low pressure refrigerated tank shells	One-half of sum of diameters of adjacent tanks					
To flammable liquid[4] storage tanks	Not less than 30 m (100 ft) between low pressure refrigerated LFG and flammable liquid tank shells, but LFG and flammable liquids must be in separate bunds					
To pressure storage vessels	As defined above under Pressure Storage					

Notes (to original table)
(1) Measured in plan from the nearest point of the vessel, or from associated fittings from which an escape can occur when these are located away from the vessel.
(2) If this distance cannot be achieved, the need for suitable fire protection of the cable or pipeline should be considered.
(3) The tanks containing water soluble non-hydrocarbons being bunded (see Clause 8.6.2), power cables and pipelines at ground level should be outside the bund and so protected by the bund from fire in the tanks.
(4) Flammable liquids are those with flashpoints up to 65.5°C (150°F).
(5) Measured in plan from the nearest part of the bund wall (see Clause 8.6.3), except where otherwise indicated.
(6) The Home Office *Code for Storage of LPG at Fixed Installations* recommends 45 m (150 ft) for C_4 as well as C_3 storage, which is considered to be unnecessarily conservative. The designer may be able to persuade the Licensing Authority of the adequacy of the ICI *Code* in this respect, in view of the significant difference in rate of vaporization of the respective materials.
Additional notes (communicated by ICI c. 1977):
(1) The separation distances quoted in this table are those within which leaks from pumps, valves, flanges, etc., will normally disperse to a safe level. They are not 'safety distances' for vapour cloud explosions.
(2) Refrigerated storage tanks are now often constructed with an outer wall of concrete which will retain any spillage. This design may permit the use of lower separation distances but no definite figure has been agreed.

Table 22.8 *Minimum recommended separation distances for LPG pressure and refrigerated storages: IP* LPG Storage Code *(Institute of Petroleum, 1987 LPG Storage Code)*

A Pressure storage

Site	*Maximum radiation flux levels*	
	(kW/m^2)	($BTU/h\ ft^2$)
Equipment		
The outer surfaces of adjacent *pressure storage vessels* (1):		
Thermally protected (2)	44	13 750
Unprotected (3)	8	2 500
The outer surfaces of adjacent storage *tanks* containing *flammable* products (4) and process facilities:		
Thermally protected (2)	32	10 000
Unprotected (3)	8	2 500
Filling/discharge points	8	2 500
Personnel inside boundary		
Process area (5)	8	2 500
Protected work area (6)	8	2 500
Work area (7)	5	1 500
Critical area (8)	1.5	500
Plant boundary		
Remote area (9)	13	4 000
Urban area (10)	5	1 500
Critical area (8)	1.5	500

B Refrigerated storage

Site	*Maximum thermal radiation flux levels*	
	(kW/m^2)	($BTU/hr\ ft^2$)
Equipment		
The outer surfaces of adjacent *refrigerated storage tanks:*		
Thermally protected (2)	32	10 000
Unprotected (3)	8	2 500
The outer surfaces of adjacent storage *tanks* containing *flammable* products (4):		
Thermally protected (2)	32	10 000
Unprotected (3)	8	2 500
The outer surfaces of adjacent LPG *pressure storage vessels* and process facilities (11)	8	2 500
Personnel inside boundary		
Process area (5)	8	2 500
Protected work area (6)	8	2 500
Work area (7)	5	1 500
Critical area (8)	1.5	500
Plant boundary		
Remote area (9)	13	4 000
Urban area (10)	5	1 500
Critical area (8)	1.5	500

Notes:

(1) The distance from an LPG *pressure storage vessel* to a *refrigerated storage tank* is determined by the requirement of Chapter 3 (see 3.3.1) and Table 2 of this appendix.

(2) Such facilities/areas are protected by means of water sprays, insulation, radiation screens or similar systems.

(3) Protection is provided by spacing alone.

(4) Special consideration should be given to the location of floating roof tanks containing high vapour pressure products since effective water cooling of their roof structures is impracticable.

(5) A normally unoccupied area occasionally manned by trained and suitably clothed persons familiar both with escape routes and opportunities for temporary shelter afforded by the process plant.

(6) A permanent building where personnel inside are shielded and/or have a shielded means of escape.

(7) An open area or small (e.g. temporary) building without a shielded means of escape.

(8) This is either an unshielded area of critical importance where people without protective clothing may be required at all times including during emergencies or a place difficult or dangerous to evacuate at short notice (e.g. a sports stadium).

(9) An area only infrequently occupied by small numbers of persons, e.g. moorland, farmland, desert.

(10) An area which is neither a remote area nor a critical area.

(11) The allowable thermal radiation flux level is restricted for these facilities in view of the potentially longer duration of exposure resulting from a *refrigerated tank/bund* fire.

Table 22.9 *Guidelines for hazardous area classification of LPG pressure storage (Health and Safety Executive, 1987 HS(G) 34) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

Factor			*Area classification*
Storage vessels	(a)	Within 1.5 m in all directions from the discharge orifice of fixed liquid level gauges, rotary or dip gauges, filler openings	Zone 1
	(b)	Up to 1.5 m above ground level and within the distances set out for a fixed source of ignition in Table 2 column (a)[b]	Zone 2
Relief valve discharge	(a)	Within direct path of discharge	Fixed electrical equipment should not be installed
	(b)	Within 1.5 m in all other directions from point of discharge	Zone 1
	(c)	Beyond 1.5 m but within 4.5 m, or the separation distance in Table 2 column (a)[b] in the case of vessels with a capacity not exceeding 2500 l, in all directions from point of discharge	Zone 2
Tanker loading and unloading	(a)	Within 1.5 m in all directions from a point where connections are regularly made or disconnected for a product transfer	Zone 1
	(b)	Beyond 1.5 m but within 4.5 m or the separation distance in Table 2 column (a)[b] in the case of vessels with a capacity not exceeding 2500 l, from point of connection or disconnection	Zone 2
Pumps, compressors and vaporizers other than direct fired			
(a) Outdoors in open air, at or above ground level[a]	(a)	Within 1.5 m in all directions	Zone 1
	(b)	Beyond 1.5 m but within 4.5 m in all directions or the separation distance in Table 2 column (a)[b] in the case of vessels not exceeding 2500 litres capacity.	Zone 2
(b) Indoor location with adequate ventilation	The entire room and any adjacent room not separated by a vapour-tight partition		Zone 1

[a] Where there is a high standard of maintenance of pumps and pump seals the area within 1.5 m in all directions from the pump may be classified as Zone 2.
[b] Of HS(G) 34.
Notes:
(1) Where any area is classified under more than one factor the higher classification should prevail.
(2) Any pit, trench or depression falling within a Zone 1 or Zone 2 area should be treated as a Zone 1 area throughout.
(3) The term 'outdoors in open air' includes pumps, compressors and vaporizers which are covered by a canopy.

the main shut-off valve, which is remotely operated and has fail-safe action, closing on air failure.

There is also an alternative arrangement in which flanged joints are allowed on the vessel side of the separation wall.

The preferred pipework arrangement for a spherical storage vessel is shown in Figure 22.8(b).

If possible, the main filling/discharge pipe should be the only one below the liquid level. Another inlet may be provided at the top of the vessel if mixing of the liquid by pumping is necessary. There may also be a vapour return line to the vessel. With a horizontal cylindrical vessel it is desirable to put the filling/discharge line and the vent at opposite ends to assist purging of the vessel.

The vessel branch sizes should be 4 in. minimum for the filling/discharge line and 1 in. minimum for all other branches.

Sections of pipe, such as those between shut-off valves, in which liquid may become trapped and may then undergo further expansion, should be provided with liquid expansion relief valves.

There should be good access to valves. Permanent access should be provided for valves which are operated or maintained regularly, or which may need to be used in an emergency.

The pipework should be protected against mechanical damage from external sources.

Pipework is very vulnerable to fire and should be protected as far as possible. Fireproof insulation on pipework near storage vessels may be appropriate.

A small fire at a leaking flange can have a torch effect and this possibility should be borne in mind in designing pipework. A fire of this type was one of the causes considered at the Flixborough Inquiry.

Remotely operated shut-off valves should be provided on all discharge or drain lines from storage vessels and these valves should be stable in fire conditions. Other valves in the storage area should be of fire-safe design.

Turning to the guidance on pipework and fittings in the main LPG codes, detailed treatments are given in the LPGA *LPG Storage Code*, the LPGA *LPG Piping Systems Code* and the IP *LPG Storage Code*. These codes cover

materials of construction, pipe thickness, pipe joints, welding, flanges, gaskets, bolts, valves, pipe supports, etc.

The LPGA *LPG Storage Code* gives detailed requirements for the minimum set of fittings on an LPG pressure storage vessel. These are (1) a pressure relief valve on the vapour space, (2) a drain or other means of emptying the vessel, (3) a maximum level indicator, (4) a filling connection, (5) a service connection, and (6) a pressure gauge on the vapour space on vessels of over 5000 l.

The *Code* requires the provision of a manual shut-off valve on all liquid and vapour connections, except on the pressure relief valve or very small diameter ($\leq$1.4 mm) connections.

Another requirement of the code is that any connection on the vessel greater than 3 mm diameter for liquid or 8 mm diameter for vapour, except that for a relief valve, should be protected with an emergency shut-off valve (ESV). The types of ESV mentioned are excess flow valves, remotely operated isolation valves and back-check valves. The detailed applications of the three types are given in the *Code*.

A back-check valve is a spring-loaded non-return valve held in the closed position. The valve remains closed against reverse flow until the upstream pressure exceeds that downstream, when the valve opens.

HS(G) 34 requires a remotely operated ESV on all liquid lines greater than 19 mm in diameter if they supply an activity which requires frequent making and breaking of connections or one where the general public have access or if the vessel is large ($\geq$225 m^3).

22.8.8 Water drainage facilities

As described in Chapter 20, small amounts of water tend to accumulate at the bottom on an LPG storage vessel and this water is commonly removed by the periodic action of an operator who drains it off manually. Loss of control by the operator can result in a breakthrough and escape of LPG.

Methods of dealing with this problem have been discussed by Klaassen (1980b), who describes valve arrangements for the bottom of LPG spheres designed to minimize the chances of such an escape. He describes a system with a 2 in. line coming out of the bottom of the sphere, reducing to $\frac{3}{4}$ in. on the downstream part of the drain line. Basic principles underlying the system are: (1) a reduction in the line size, as just mentioned; (2) the installation of a first ball valve in the 2 in. line dedicated to isolation rather than manipulation, and preferably remotely controlled; (3) the provision of two further ball valves on the drain line, the downstream one being a spring-loaded valve; (4) a separation between the drain valve and the drain funnel; and (5) the provision of an indication of water level which is visible at the point where the draining operation is performed.

Guidance on water draining arrangements is given in HS(G) 34 *The Storage of LPG at Fixed Installations* (HSE, 1987) as follows:

> 66. Drain connections should be less than 50 mm in diameter and fitted with two shutoff valves in series. The length of piping between the valves should be at least 0.5 m to minimize the risk of simultaneous obstruction of both valves by the freezing of any water present in the LPG. The piping downstream of the second valve should not discharge beneath the vessel. The second valve and piping should be adequately supported and secured to prevent mechanical damage or breakage by vibration or jet forces. Both valves on the drain systems should have means of actuation which cannot be readily removed or moved from the closed position except by intentional operation.
>
> 67. Alternatively, a satisfactory arrangement for drain lines could be a single valve and a plug or blanking plate fitted on the discharge side of the valve. Additional pipework should be fitted, when required, in accordance with paragraph 66.
>
> 68. No drain lines should discharge within 6 m of any drainage system where this would be liable to create a hazard.

22.8.9 Ancillary facilities

The ancillary facilities required for LPG pressure storage include, in particular, pumps and vaporizers. It is important that these items, which effectively introduce a process element, should not hazard the storage. A pump should not be located directly under a vessel.

Pumps are a potential source of leakage of flammable vapours. This is particularly the case for pumps with packed glands. Pumps with mechanical seals are to be preferred. The type of pump used also has implications for the hazardous area classification.

A positive displacement pump needs to have a bypass or other appropriate protection against overpressure. The thermal expansion of LPG in a pump which is isolated and is then started up can be particularly damaging.

LPG storage is often provided with vaporizers. Descriptions of, and requirements for, vaporizer systems are given in NFPA 58 and 59, the LPGA *LPG Storage Code* and HS(G) 34. Vaporizers may be heated by direct firing or by an indirect heating medium such as steam or hot water. Some principal features of a vaporizer system include the vaporizer itself, drain connections, pressure relief and instrumentation. Direct fired and certain other types of vaporizer constitute ignition sources.

22.8.10 Instrumentation

An LPG pressure storage vessel should be provided with suitable measurements and alarms on liquid level, pressure and temperature. A discussion of instrumentation for LFG pressure storage is given in the ICI *LFG Code*. Instrumentation is essential to the safe operation of LPG pressure storage. It is important both that the instruments function correctly and that they do not themselves hazard the process.

Vessels should be protected against maloperation by alarm and trip systems. Overpressure is obviously one condition against which protection is necessary. It is often caused by overfilling, and so high level alarms and trips are important. But this is not the only condition requiring protection – overtemperature and undertemperature are important too.

The measurement of level in pressure storage may present some difficulties. In order to avoid leakage, it may be policy not to put additional branches on the vessel simply for level measurement, which rules out conventional differential pressure measurements. The *Code* recommends duplicate internally mounted level

measuring instruments as the primary measurements with a magnetic float gauge or radioactive gauge as the secondary measurement. Separate high and low level switches are also required for the alarm and trip systems. Here the *Code's* recommendation is that the switch should be put in an externally mounted float chamber, the top connected to the top of the storage vessel and the bottom to the filling/discharge line between the ball valves and the manifold.

Debris from instruments should not create a hazard. It may be necessary to take precautions to prevent a loose float from a level measuring device blocking the branches to the relief valves.

For the measurement of temperature, a long thermocouple pocket is recommended. It should be inserted from the top and reach the bottom so that the temperature at any level can be measured. The bottom of the pocket should be guarded or supported in some way to reduce the risk of fracture by vibration.

Specific instrumentation requirements are contained in the main LPG codes, particularly in respect of level gauging. The LPGA *LPG Storage Code* requires the installation of a fixed maximum liquid level device, which should be of the type that allows vapour or liquid to be bled from a valve attached to a dip-tube to indicate when the maximum permitted level is reached during filling. The connection through the vessel should be no larger than 1.4 mm in diameter unless an excess flow valve is fitted. For a vessel of more than 5 m^3 capacity the *Code* also requires the provision of a pressure gauge connected to the vapour space. It requires that the connection be protected either by a tapping reduced internally to a bleed hole not larger than 1.4 mm or by a suitable excess flow valve or shut-off valve.

The provision of a contents gauge is also advised. The IP *LPG Storage Code* suggests that consideration be given to the installation of two independent level gauges in addition to the maximum level device.

Sampling is another aspect which merits careful attention, because it tends to be a source of leakage. The *ICI LFG Code* makes the following recommendations on this. Sampling should be done from pipelines rather than from vessels. If a representative sample is required from a vessel, the product should be circulated and a sample taken from the circulation line. Sample points should be carefully sited with respect to hazardous area classification, safe disposal of vented samples and access.

Sample connections should be limited, preferably to 1 in. reducing to $\frac{1}{4}$ in. There should be double manual isolation with a 1 in. ball valve followed by a $\frac{1}{4}$ in. valve. The valves should be close together but with a minimum separation of 1 m to avoid simultaneous blockage of both valves by ice or hydrate.

Operations involved in sampling were considered in Chapter 20.

Gas, flame and smoke detectors are another important aspect of instrumentation for storage. These have been discussed in Chapter 16.

22.8.11 Pressure relief

A pressure storage vessel should be protected against overpressure by a pressure relief valve. Pressure relief valves have been discussed in detail in Chapter 12. Only those aspects relevant to storage are considered here.

Pressure relief valves for LPG pressure storage vessel should be designed according to a recognized code such as BS 5500: 1991 or the ASME *Boiler and Pressure Vessel Code*, *Section VIII*. In this particular case, other appropriate codes are the LPGA *LPG Storage Code*, API RP 520 and NFPA 58 and 59.

Protection is required against overpressure due to (1) abnormal operating conditions and (2) fire exposure. It may be provided by a single pressure relief valve or by separate relief valves for each category.

Operational relief

A pressure relief valve for abnormal operating conditions should be designed to handle the most severe conditions which are likely to arise. Typical abnormal operating conditions include overfilling, high rundown liquid temperature, and high tank temperature due to solar radiation.

Overpressure due to abnormal operating conditions may develop slowly or suddenly. The most common cause of a rapid increase in pressure is overfilling. The worst case here is obtained by considering the maximum liquid flow obtainable through the fully open control valve, and bypass if fitted, on the supply line.

Fire relief

A pressure relief valve for fire exposure should be designed to deal with the vapour generated by this. The vapour generated may be calculated from the latent heat of the liquid and from the heat input.

There are a number of measures which can, in principle, reduce the heat absorbed during a fire and hence the quantity of vapour to be handled. The most basic is to slope the ground under the vessel so as to ensure that any flammable liquid spill is drained away. Other measures to reduce heat absorbed include fireproofing, depressurization and water sprays.

A method of estimating the heat absorbed in a fire is given in API RP 520, Appendix D. For a bare surface two equations are given:

$$Q = 21\,000\,FA^{0.82} \qquad [22.8.1]$$

and

$$Q = 34\,500\,FA^{0.82} \qquad [22.8.2]$$

where A is the total wetted surface (ft^2), F is an environmental factor and Q is the total heat absorption (BTU/h). Equation 22.8.1 is applicable where there is adequate drainage and prompt fire fighting, and Equation 22.8.2 where these conditions are not met.

In this method, any credits allowed for other measures are incorporated in the environmental factor F. The value of F is unity for a bare vessel. No credit is given for depressurization or water application facilities, and even with these the value of F is still unity. Credit is given, however, for fireproof thermal insulation, provided it will resist dislodgement by fire hose streams. For a vessel furnished with fireproof insulation with a thermal conductance of 4 BTU/ft^2 h °F the value of F is 0.3. Lower values of F are given for insulation with lower thermal conductances.

The LPGA *LPG Storage Code* and NFPA 58 and 59 give pressure relief valve capacities in tabular form and

also give an equation for large vessels. The LPGA *Code* states that these capacities cover fire relief.

The pressure relief valve setting, both for operational and for fire relief, is considered in Chapter 12, and valve sizing is discussed in Chapter 15. For pressure storage, valves should be able to handle flashing, two-phase flow.

Combined relief

A single pressure relief valve may be used to provide both operational and fire relief. Alternatively separate valves may be used for operational and fire relief.

The arrangements are discussed in the ICI *LFG Code*. The *Code* states that where there is a single pressure relief valve, the relieving capacity should be at least equal to the greater of the individual capacities required for operational and fire relief, and that where separate operational and fire relief valves are provided the combined capacity of the two valves may be set against the fire relief requirement.

Fluid phase

A discussion of the fluid phase during pressure relief is given in API RP 520, although the account is not specifically concerned with storage. The IP *LPG Storage Code* states that for overfilling the relief discharge would be a flashing liquid, whilst for fire relief it treats the discharge as a vapour.

Relief disposal

A discussion of relief disposal for LFG storage vessels is given in the ICI *LFG Code*. The *Code* states that it is preferable that relief valves, whether for operational or fire relief, should discharge into a closed system.

An operational relief valve should discharge into a closed system which is led to an atmospheric vent or to a flare. The closed system should be designed to handle liquid discharge and to take the full flow from the valve. A fire relief valve should also discharge to a closed system. If this is not practical, it can be discharged vertically upwards to the atmosphere via a vent pipe.

Direct discharge to atmosphere should be done in such a way as to ensure that flammable material is diluted below its lower flammability limit before it reaches an ignition source, and toxic material should be below the appropriate exposure or odour limit before it reaches ground level outside the plant area.

These requirements for direct discharge are fairly readily met for vapours lighter than air which can be vented at a point above plant structures at low velocities, but for those heavier than air it is more difficult. The *Code* states that for vapours heavier than air it is necessary to use a velocity of at least 150 m/s (500 ft/s) to ensure jet mixing with air sufficient to give rapid dilution. The problem is discussed by Cude, who indicates that current experience is that this criterion can be reliably met only by the use of pilot-operated relief valves rather than ordinary relief valves. A fuller account of dispersion from relief valves is given in Chapter 15.

Most LPG pressure storage vessels are fitted with vertical vent pipes so that the relief discharge is directed upwards. The LPGA *LPG Storage Code* states that a vent pipe should have its outlet at least 1.8 m above the top of the vessel and should be not less than 3 m above ground level. HS(G) 34 gives similar requirements, but states that for large vessels the pressure relief system may discharge to the vent collecting system of a flare.

22.8.12 Vacuum protection

In severe cold weather the temperature of the contents of an LPG pressure storage vessel may fall below 0°C. For the storage of commercial butane in particular, this can cause the vapour pressure of the liquid to fall below atmospheric and thus create vacuum conditions.

This problem and the measures that can be taken to protect against it are discussed in the LPGA *LPG Storage Code*. The *Code* states that, in the absence of more specific information, a butane vessel should be designed for a minimum temperature of −18°C, which is the lowest ambient temperature recorded in the UK as sustained over a period of 12 hours.

One approach is to design for full vacuum. Alternative approaches are (1) the prevention of unacceptable vacuum conditions, (2) the provision of high and low pressure alarms, and (3) the use of methods based on product composition or vacuum breaking.

A low pressure alarm serves to give warning of the development of vacuum conditions.

Two methods of preventing an unacceptable vacuum are hot gas return and propane vapour pressurization. Hot gas return involves feeding hot butane vapour from a local vaporization source, and propane vapour pressurization involves connecting the vapour space of the butane vessel to that of a local propane storage vessel or to propane cylinders. Details of the procedures to be used are given in the LPGA *Code*.

In certain special cases, and by agreement with the supplier, the composition of butane to BS 4250: 1987 may be controlled so that the vapour pressure at the lowest service temperature will be above the minimum design pressure of the vessel. It should be confirmed that at this composition the vessel can withstand the vapour pressure at the reference temperature.

Other methods of limiting vacuum are the use of vacuum breakers or the introduction of inert gas. Both methods tend to lead to operating problems due to the introduction of air or inert gas and the first particularly is a specialist matter.

22.8.13 Vaporizers

LPG in vapour form may be obtained from a pressure storage installation using a vaporization facility. Vaporizers for LPG are treated in HS(G) 34.

LPG vaporizers may be heated with low pressure steam or hot water or heated electrically or by direct firing. The equipment should be located with suitable separation distances, in a well ventilated location and with the ground sloped to drain away any leak to a safe place.

HS(G) 34 gives the following minimum separation distances between vaporizers and the nearest important buildings or line of adjoining property. For vaporizers of capacity up to 36 kg/h, 3 m; of capacity >36 to 227 kg/h, 7.5 m; and of capacity >227 kg/h, 15 m. Separation distances between LPG vessels and direct fired or non-explosion protected electrically heated vaporizers are as given in column 3 of Table 22.6, which gives the distances for sources of ignition. The separation distance from LPG vessels for other types of vaporizer is 1.5 m.

Other features detailed in HS(G) 34 include the arrangements for draining, pressure relief and control of liquid level and temperature.

22.8.14 Fire protection

Fire prevention and protection of LPG pressure storage is dealt with in the main codes mentioned and also specifically in *Recommendations for Prevention or Control of Fire Involving LPG* (LPGA, 1972 COP 3) (the LPGA *Fire Code*). A further relevant standard is BS 5908: 1990. Other accounts include those by Kletz (1977d), Fullam (1987), Nazario (1988), Schoen and Droste (1988) and Schoen, Probst and Droste (1989).

The effect of fire on a pressure vessel is broadly similar to that on an atmospheric tank. The unwetted parts of the vessel become hot and lose strength. As a result the vessel may burst, even though it is below its design pressure. Overtemperature is just as serious as overpressure. The loss of strength is greater with vessels designed to advanced pressure vessel codes.

The other effect of fire is to heat the liquid in the vessel so that the pressure rises and causes the pressure relief valve to lift. Further heat input causes the liquid to vaporize without further rise in pressure, provided the valve has enough capacity to vent the vapour. If the valve fails to operate or has insufficient capacity, the rise in pressure may burst the vessel.

Failure of a pressure vessel in a fire may therefore be due to either overtemperature or overpressure. The failure of the vessel at Feyzin, for example, occurred due to overtemperature, even though the relief valve had lifted.

A discussion of fire prevention and protection is given in the ICI *LFG Code*. Some of the measures given in the *Code* have already been discussed, such as diversion and fire walls (see Section 22.8.5), fire protection of pipework and fittings (see Section 22.8.7) and fire and gas detection systems (see Section 22.8.10).

The ICI *Code* specifies measures to minimize spillages. The vessels and pipework should be made to give high standards of safety in both normal and emergency operations, by appropriate design calculation methods. The number of connections below the top liquid level should be kept to a minimum, preferably just one filling/discharge line if possible. The minimum size connections should be used for draining and sampling. The installations should be protected against external damage from such sources as vehicles and other plants. There should be good level measurement and other control instrumentation, and attention should be paid to the filling arrangements.

Measures for controlling spillages are also specified. The basic principle is that any vapour cloud resulting from a spillage should be safely diluted by air below its lower explosive limit before it can find a source of ignition. This dispersion should preferably be effected by air movement but, if necessary, some form of barrier may be required to contain and disperse the cloud.

Thus the installation should be sited with regard to factors such as ground contours and the prevailing wind. The provision of gas detectors should be considered. If necessary, consideration should be given to the provision of barriers or steam curtains to contain, direct or disperse the vapour cloud. Attention should be given to possible sources of ignition.

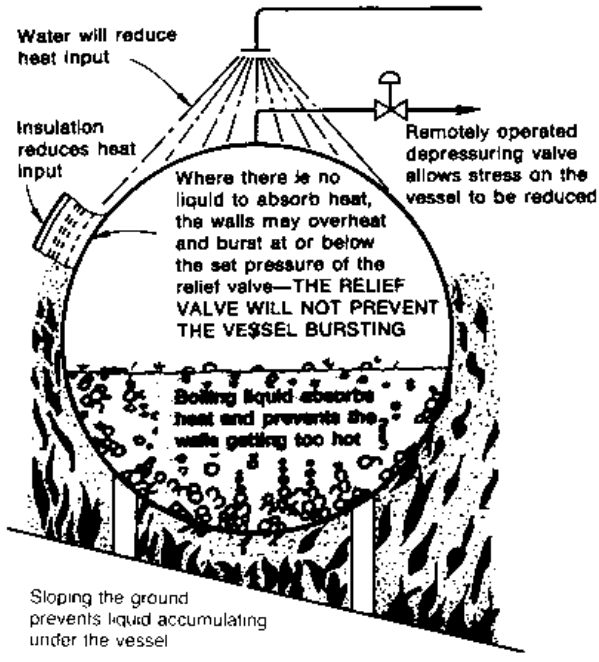


Figure 22.10 *Fire protection arrangements for an LPG pressure storage sphere (Kletz, 1977d) (Reproduced with permission from* Hydrocarbon Processing*, August, 1977)*

Finally, the *Code* specifies measures for controlling fire. The layout should ensure that liquid spillages are drained away from under vessels to a catchment area where they can be pumped out or burned. Vessels should be provided with water cooling or fireproof insulation and supports should be fireproofed. Consideration should be given to the provision of fire fighting equipment to control and extinguish burning hydrocarbon liquids.

Figure 22.10 shows a classic diagram by Kletz (1977d) of the methods of fire protection for an LPG pressure storage vessel. They are (1) sloping of the ground beneath the vessel, (2) fire insulation, (3) a remotely operated depressurization valve, (4) water sprays, and (5) a pressure relief valve.

Fixed water sprays are effective in giving immediate cooling of exposed surfaces and are widely used. On both horizontal cylinders and spheres there is a tendency for water to come off the vessel at the 'equator' and therefore sprays are usually provided both above and below this line.

The ICI *LFG Code* gives the following method of calculating the amount of water required. For a vessel enveloped in fire the rate of application of water needed to remove the total heat input is 0.2 UKgal/ft^2 min. But for a vessel designed to the *Code*, a lower rate of application in the range 0.06–0.2 UKgal/ft^2 min is acceptable, provided the ground beneath the vessel is impervious and sloped away to a catchment area and the pipework is carried beyond the vertical projection of

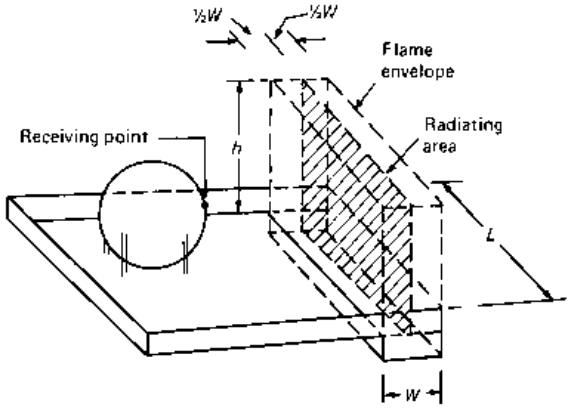


Figure 22.11 *Heat radiation from a fire burning in a catchment area to a pressure storage vessel (ICI/RoSPA 1970 IS/74; reproduced by permission)*

the vessel with no flanges or other fittings beneath the vessel.

The rate of application of water may be determined by heat flux calculations and from the rise in the temperature of the water from the mains temperature to a temperature close to boiling point at 100°C.

The *Code* gives the following method for the calculation of the heat flux. It is assumed that the separation distances given earlier in Table 22.7 are observed and that the fire is in the catchment area as shown in Figure 22.11. Then the heat radiated and the intensity of heat radiation from the flame burning on the liquid pool are calculated from the equations

$$Q = 5.1 \times 10^{-5}\, LW\rho C \qquad [22.8.3]$$

$$I = \frac{2.5 \times 10^{-5}\, LW\rho C}{(L+W)h + LW} \qquad [22.8.4]$$

where C is the net calorific value of the liquid in the pool (kJ/kg), h is the height of the flame ($= 2W$) (m), I is the intensity of heat radiation from the flame envelope (kW/m^2), L is the length of the pool (m), Q is the heat emitted by fire (kW), W is the width of pool (m) and ρ is the density of the liquid (kg/m^3).

It is assumed that the heat is radiated from a radiating area which is a vertical rectangular plane through the centre line of the flame envelope cube prism parallel to the nearest point on the equator of the vessel, as shown in Figure 22.11. The heat flux received by this vessel is obtained by using the view factor method.

A fixed water spray system is normally maintained dry so that it cannot become frozen. When this system is required to operate, water is supplied by a deluge valve. This valve may be operated manually or automatically. If operation is manual, the valve should be in a place accessible during the fire. The preferred system, however, is automatic operation triggered by fire detectors.

Automatic detectors should be fast acting in order to protect the pipework in particular. Manual override control should be provided on an automatic system to allow sprays to be turned on to protect adjacent surfaces, even though the automatic controls have not brought them on.

It is desirable that, if possible, only those fixed sprays are activated which contribute to dealing with the fire concerned. Large installations should be subdivided to conserve water, which is likely to be needed to fight the fire. Again the main water sprays are normally provided by mobile equipment and are used both to fight the fire and to cool exposed surfaces.

Fireproof thermal insulation may be used on pressure vessels as an alternative to, or in addition to, fixed water sprays. Such insulation reduces the rate of heat input from a fire to the vessel and this lag gives time in which fire fighting measures such as mobile water sprays may be brought into play and the fire extinguished, or in the worst case an evacuation organized.

Fireproofing should be such as to provide protection for 2 hours before the vessel becomes dangerously overheated. This insulation should be designed in conjunction with the arrangements for fire pressure relief. A fireproof insulation suitable for this purpose may be obtained by the use of vermiculite cement with a minimum thickness of 2 in.

Some of the measures described have their difficulties. The use of fire insulation is not straightforward. Some of the problems are considered by Fullam (1987). The use of such insulation inhibits inspection of the vessel. Corrosion and water ingress are liable to occur. There are potential problems with the durability of the insulation and its resistance to water jets. He states that these problems are serious enough to prevent the general adoption of this measure.

Likewise, the use of depressurization is controversial, as discussed by Nazario (1988). One problem is the time required to depressurize. Another is that the depressurization lowers the liquid level and increases the area of unwetted metal exposed to the fire. The approach described by Nazario is to use fire insulation as the preferred method for horizontal storage vessels, but not for spheres. On the other hand, water sprays and not insulation are used for spheres.

Turning to the guidance on fire prevention and protection in the main LPG codes, and also specifically in the LPGA *Fire Code*, detailed treatments are given in API Std 2510, AP RP 520, NFPA 58 and 59, the LPGA *LPG Storage Code*, the IP *LPG Storage Code* and HS(G) 34.

The LPGA *LPG Storage Code* gives a summary table of fire protection arrangements for storages of different sizes. For storages below 25 te it is generally sufficient to provide a water supply; for storages greater than 25 te but less than 50 te, fixed or portable water monitors should be available; and for storages greater than 50 te there should be a fixed water spray installation. This system should be automatic unless the plant is continuously attended.

With regard to the wetting rate required to effect protection for an uninsulated vessel, the *Code* states that a full film of water needs to be established over the whole vessel surface and supports at a rate of 7 l/m^2 min, and that the typical design spray rate required to achieve this is 9.8 l/m^2 min; the *Code* refers to the work of Billinge, Moodie and Beckett (1986). In some cases, one of these figures is quoted without the other;

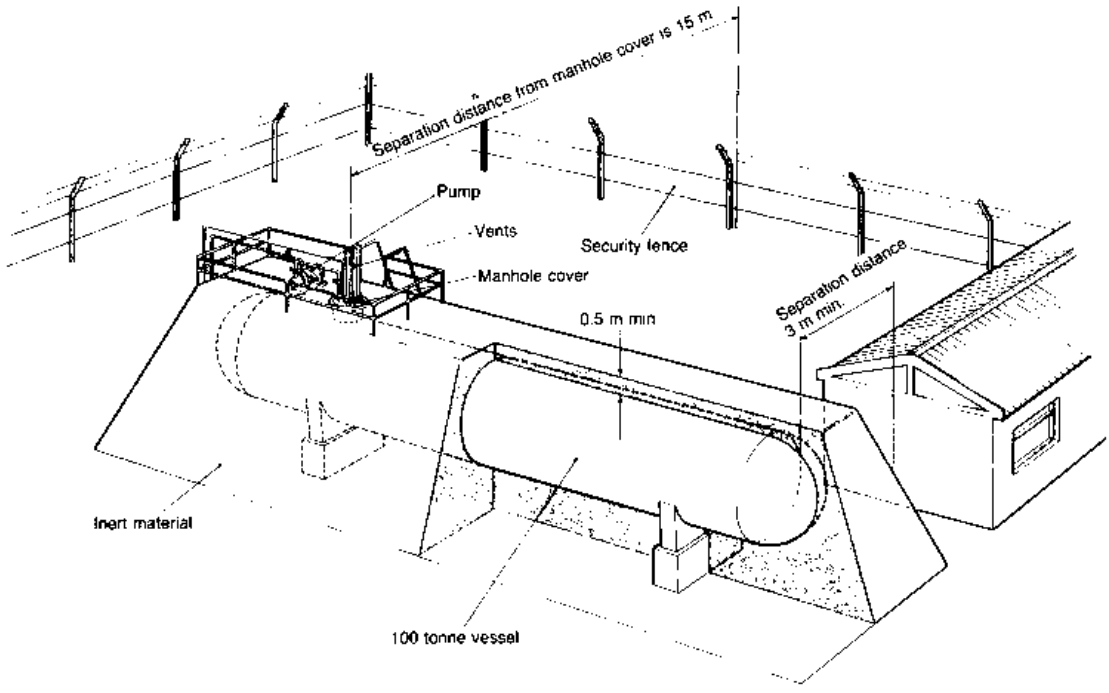


Figure 22.12 *General arrangement of LPG mounded pressure storage vessel (Health and Safety Executive, 1987 HS(G) 34) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

the IP *LPG Code* refers to the lower figure and HS(G) 34 to the higher one.

There should be adequate drainage to remove the fire water, and where necessary water sealed interceptors should be provided to prevent LPG entering the storm drains.

The LPGA *LPG Storage Code* recognizes fire insulation as an alternative to water sprays, provided it is capable of limiting the vessel temperature below 450°C for a period of at least 60 minutes in full fire engulfment. The *Code* requires, however, that the insulation should: (1) be non-corrosive to the vessel surface; (2) be impervious to water vapour, either by cellular construction or by provision of an effective vapour barrier; (3) be resistant to a hose directed jet; (4) be durable and easily repairable, and strong enough that minor mechanical damage will not destroy the vapour barrier; (5) be unaffected by environmental conditions; and (6) not itself be a hazard, by spalling, spreading flames or emitting toxic fumes.

The LPGA *Fire Code* deals particularly with fire fighting of LPG fires.

HS(G) 34 gives guidance similar to that in the LPGA *LPG Storage Code*, again with a summary table of fire protection measures.

22.8.15 Inspection

Pressure storage vessels for LPG should be inspected in the manner and at the frequency given in the relevant codes, as described in Chapter 19.

22.8.16 Mounded storage

LPG is also stored in pressure vessels set in earthen mounds. Accounts of this method of storage are given in HS(G) 34 and by Bonnafous and Divine (1986) and Bellani, Cannalire and Beltrame (1992).

The arrangements for a mounded LPG horizontal cylindrical pressure storage vessel given by the HSE in HS(G) 34 are shown in Figure 22.12. The external surface of the vessel should be given an external coating to prevent corrosion. It should be placed on a firm foundation and installed so as to prevent movement or flotation. The backfill material should be inert and free of material likely to damage the external coating. The HSE advise that the depth of cover be at least 0.5 m.

Some of the installations of mounded LPG vessels are very large. Bonnafous and Divine describe mounded storages with horizontal pressure vessels of capacity 3 500 m^3. In these systems the vessel is supported on a compacted sand bed in a 120° circular cradle. The depth of cover is one metre minimum.

Mounded storage offers enhanced protection against external fire, thus avoiding: a boiling liquid expanding vapour explosion (BLEVE); external explosion; impact from external threats such as vehicles or aircraft; and sabotage.

22.8.17 Hydrogen related cracking

In certain circumstances LPG pressure storage vessels are susceptible to cracking. The problem has been described by Cantwell (1989 LPB 89). He gives details of a company survey in which 141 vessels were

inspected and 43 (30%) found to have cracks; for refineries alone the corresponding figures were 90 vessels inspected and 33 (37%) found to have cracks.

The cracking has two main causes. In most cases it occurs during fabrication and is due to hydrogen picked up in the heat affected zone of the weld. The other cause is in-service exposure to wet hydrogen sulphide, which results in another form of attack by hydrogen, variously described as sulphide stress corrosion cracking and hydrogen assisted cracking.

LPG pressure storage has been in use for a long time and it is pertinent to ask why the problem should be surfacing now. The reasons given by Cantwell are three aspects of modern practice. One is the use of higher strength steels, which are associated with the use of thinner vessels and increased problems of fabrication and hydrogen related cracking; the use of advanced pressure vessel codes, which involve higher design stresses; and the greater sensitivity of the crack detection techniques available.

He refers to the accident at Union Oil on 23 July 1984 in which 15 people died following the rupture of an absorption column due to hydrogen related cracking (Case History A111). Cantwell states: 'The seriousness of the cracking problems being experienced in LPG vessels cannot be overemphasized'.

The steels most susceptible to such cracking are those with tensile strengths of 88 ksi or more. Steels with tensile strengths above 70 ksi but below 88 ksi are also susceptible.

Cantwell also describes measures for the avoidance of the problem. For new vessels he recommends the use of lower strength steels which have controlled chemistry and welding and post-weld heat treatment and which have good toughness both at ambient and low temperatures. For existing vessels the recommendations centre on inspection techniques and intervals and on repair methods. A measure applicable to both cases is the elimination of breakthrough of wet hydrogen sulphide into LPG rundown.

22.8.18 LPG-air plants

LPG storage may be associated with an LPG–air plant, which is an installation for the production of LPG–air mixtures. Such plants are covered by the *Recommendations for LPG–Air Plants* (LPGA, 1972, COP 9). The main elements of such plant are pumps and vaporizers.

22.9 LPG Storage: Refrigerated Storage

Codes and standards for LPG deal mainly with pressure storage rather than with refrigerated storage, but the guidance in NFPA 59 does cover refrigerated storage. Other guidance is available which deals primarily with storage tanks for low temperature duty. Further information may be sought in codes for refrigerated storage of LNG.

22.9.1 Storage tanks

Tanks for the refrigerated storage of LPG and LNG have developed from those for atmospheric storage of petroleum products. A relevant British Standard is BS 4741: 1971 *Specification for Vertical Cylindrical Welded Steel Storage Tanks for Low-temperature Service: Single-wall Tanks for Temperatures down to* $-50^{\circ}C$.

There is available a variety of tank systems which may be used for the storage of LPG or LNG. A more detailed account is deferred to Section 22.11 on LNG, and only a brief account is given here.

Tank systems for LPG have been described by Morand, Claude and Herbretau (1985). They distinguish the following tank systems: (1) single wall tank, (2) double wall tank, (3) double integrity tank and (4) membrane tank.

A single wall tank has a wall made of low temperature steel with external insulation covered by a vapour barrier. A double wall tank has an inner wall of low temperature steel and an outer wall of carbon steel with insulation in between. The outer wall is not designed to withstand the cold liquid, so that this system still gives only a single effective containment. A double integrity tank system has an inner tank of low temperature steel with a suspended deck and an outer wall either of low temperature steel or pre-stressed concrete, but in either design the outer wall also is capable of containing the cold liquid. The membrane tank consists of a pre-stressed concrete containment with an aluminium foil membrane. These four tank systems are shown in Figure 22.13.

Morand, Claude and Herbretau have given a detailed account of the GMS 2000 membrane tank system, adapted from the GMS membrane tank system developed for marine use. In such a membrane system the functions of mechanical strength and leak-tightness are separated and are provided by separate features.

The minimum design temperature for refrigerated storage tanks should take account of the lowest temperature to which they may be subjected. The tank may be cooled down to the minimum temperature of the refrigeration system if there is little movement of the contents, or even lower if there is malfunction of the system.

22.9.2 Separation distances

Separation distances for refrigerated LPG storage are given in the IP *LPG Code* and NFPA 59, and also in the ICI *LFG Code*.

22.9.3 Secondary containment

Secondary containment for refrigerated LPG storage tanks is treated in the same codes. An LPG storage tank should be provided with a full bund. The typical LPG refrigerated storage tank is sufficiently large to have its own bund, but in any event tanks containing other materials should not be located in the same bund as one holding refrigerated LPG.

If the topography is such, either naturally or by addition of diversion walls, that any spill can be contained and drained to an impounding basin, this provides an acceptable alternative to a bund.

Walls for full bunding should not be so high as to hinder fire fighting. The ICI *LFG Code* suggests a maximum height of 2 m (6 ft 6 in.) with an allowance of 0.15 m (6 in.) freeboard above the predicted liquid level. This leaves room for a foam blanket. There should be a minimum of two access points on opposite sides of the bund to allow safe access/escape in all wind

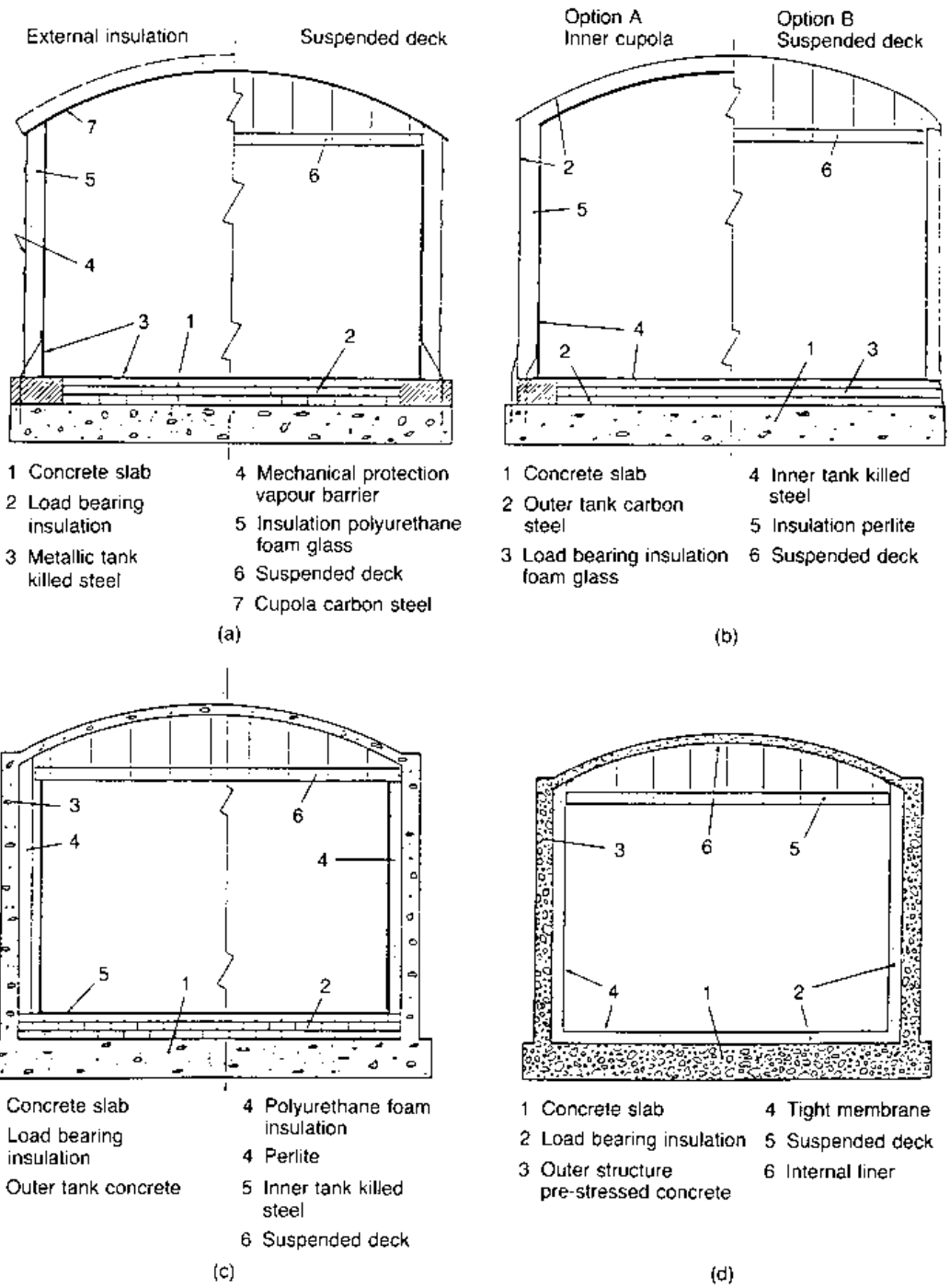


Figure 22.13 *LPG refrigerated storage tanks (Morand, Claude and Herbretau, 1985): (a) single wall tank; (b) double wall tank; (c) double integrity tank with concrete outer wall; (d) membrane tank (GMS 2000) (Courtesy of Gastech)*

directions. Access may be provided by steps over the bund.

22.9.4 Foundations

Refrigerated LPG storage tanks require good foundations and insulation for the bottom of the tank. The foundations need to be protected against 'frost heave'. The usual method of construction is to insulate the bottom of the tank and support it on a structure which has only limited contact with the ground and gives good air circulation. An account of foundation systems used for refrigerated storage tanks is given in Section 22.12.

22.9.5 Insulation

Refrigerated LPG storage tanks are insulated to reduce heat inleak.

On a single wall tank the insulation over the walls and roof is typically polyurethane foam (PUF). The insulation between the two walls of a double wall tank is usually perlite. The insulation between the walls of a double integrity tank may be PUF or perlite. A load-bearing foam glass insulation is used between the bottom of the tanks and the foundation.

Important features of the insulation on a single wall tank are the vapour sealing and the fire resistance. Vapour sealing of the insulation is necessary to prevent ingress of humid air and the consequent ice formation. The thermal insulation may also be given a degree of fire resistance, as described below.

22.9.6 Ancillary facilities

Ancillary facilities for refrigerated LPG tanks include the refrigeration system, the pumping facilities and vaporization equipment.

Reciprocating compressors are used for the direct reliquefaction of vapour boiled off due to heat inleak. Use is also made of reciprocating compressors on refrigeration sets. Malfunction of a refrigeration set can cause the liquid refrigerated to be cooled below its normal temperature.

Reciprocating compressors can be a source of leakage of flammable vapour. They are subject to crankcase explosions and should normally be protected against this by an explosion relief valve.

Pumps should not normally be located inside a bund, where they introduce an additional hazard and are themselves at risk. It is desirable to locate them outside the bund. This also allows them to be used to pump down the storage tank during a fire.

22.9.7 Instrumentation

A refrigerated LPG storage tank should be provided with suitable measurements and alarms on liquid level, pressure and temperature and on boil-off gas flow.

Principal features of the instrumentation are the arrangements to prevent overpressure and overfilling. Pressure control is an integral part of the refrigeration system.

22.9.8 Pressure relief

The tank also requires pressure relief and vent disposal arrangements. There should be arrangements for both pressure relief and vacuum relief. Details of pressure relief systems are given in NFPA 59.

22.9.9 Vaporizers

Refrigerated LPG storage is commonly equipped with a vaporization facility to supply LPG in vapour form. An account of vaporizers for LPG has been given in Section 22.8.

22.9.10 Fire protection

Fire protection for refrigerated LPG storage tanks has much in common with that for other types of storage tank for flammable products. The effect of fire on a refrigerated storage tank is basically similar to that on an ordinary atmospheric tank, but the heating and vaporization of the liquid are much more rapid.

Guidance on fire protection is given in NFPA 59. This refers to the need for hazardous area classification, for flammable gas detection and to a range of fire control and extinguishing systems such as water sprinkler, foam and dry chemical systems.

Passive fire protection for refrigerated LPG storage tanks is discussed in the ICI *LFG Code*. Tanks are provided with conventional thermal insulation, such as cork, polyurethane or perlite. Cork is combustible, but only burns slowly. In a fire risk area it is usually vapour sealed with fire resistant mastic. Polyurethane is used in a similar way, and the 'high char' variety gives significant fire protection. Perlite is non-combustible, but needs to be contained in a steel jacket not easily damaged by fire. The conventional insulation, therefore, furnishes appreciable fire protection. A further fireproof finish may be added to bring the fire resistance up to a minimum of 2 hours.

Such fire resistant thermal insulation provides a basic protection, which may be supplemented by fixed and mobile water sprays. Insofar as the insulation buys time for active fire fighting, automatic initiation of a fixed spray system may be less necessary.

22.9.11 Inspection

There is relatively little published on the inspection of, and inspection intervals for, refrigerated LPG storage tanks.

22.9.12 Underground storage

A number of installations have been built in which LNG is stored underground in an earth pit, as described in Section 22.10. The performance of these storages has been unsatisfactory and the method has essentially been abandoned. LPG may, in principle, be stored in a similar manner, but the same difficulties apply.

22.10 LNG Storage

22.10.1 Regulatory requirements

The storage of LNG is governed by the NIHHS Regulations 1982 and the CIMAH Regulations 1984. The NIHHS notifiable inventory is 50 te. The CIMAH inventory for which demonstration of safe operation may be required (Regulation 4) is 50 te and that which attracts a safety case (Regulation 7) is 200 te.

22.10.2 LNG composition

LNG is not a homogeneous material. There are appreciable differences in composition between LNGs from

different sources. Chatterjee and Geist (1972) give the properties of typical LNGs as follows:

Source	*Composition*								
	N_2	C_1	C_2	C_3	C_4	C_{5+}	SG	α	β ($^oF^{-1}$)
US	0.40	95.90	2.70	0.40	0.30	0.30	0.440	0.62	0.00164
Algeria	1.70	87.00	7.90	2.30	0.80	0.30	0.474	0.59	0.00151
Libya	0.40	68.60	24.20	9.40	2.00	0.40	0.538	0.50	0.00125

In the above table, C_4 denotes nC_4 and iC_4. The coefficients of expansion of the liquid with respect to concentration and temperature, α and β, respectively, are given by $\alpha = (1/\rho)(\delta\rho/\delta x)$ and $\beta = (1/\rho)(\delta\rho/\delta T)$, where T is the absolute temperature, x is the mole fraction of methane and ρ is the density of the liquid.

For LNGs having a molecular weight in the range 16–24, the specific gravity lies approximately in the range 0.42–0.54, respectively.

22.10.3 Storage conditions

LNG is generally stored fully refrigerated at -161^oC and at atmospheric pressure.

22.11 LNG Storage: Refrigerated Storage

22.11.1 Storage tanks

As stated earlier, tanks for the refrigerated atmospheric storage of LNG have been developed from the conventional atmospheric storage tanks. The design of atmospheric storage tanks is governed by API Std 620: 1990 *Design and Construction of Large, Welded, Low-pressure Storage Tanks* and API Std 650: 1988 *Welded Steel Tanks for Oil Storage*. For refrigerated storage frequent reference is made to API Std 620, Appendix Q: *Low-pressure Storage Tanks for Liquefied Hydrocarbon Gases* and Appendix R: *Low-pressure Storage Tanks for Refrigerated Products*. A relevant British Standard is BS 5387: 1976 *Specification for Vertical Cylindrical Welded Steel Storage Tanks for Low-temperature Service: Double-wall Tanks for Temperatures down to* -196^oC.

Tank systems for LNG have been described by Aarts and Morrison (1981), Nassopoules (1982), Closner and Wesson (1983), Collins *et al.* (1983), Steimer (1983), Gilbert *et al.* (1985), D.A. Jones (1985), Crawford, Durr and Handman (1986) and Morrison (1987). The following tank systems may be distinguished: (1) single wall tank, (2) double wall tank, (3) double integrity tank and (4) membrane tank.

A single wall tank has a wall made of low temperature steel with external insulation covered by a vapour barrier. A double wall tank has an inner wall of low temperature steel and an outer wall of carbon steel with insulation in between. The outer wall is not designed to withstand the cold liquid, so that this is still only a single containment system. A double integrity tank system has an inner tank with a suspended deck and an outer wall. Three permutations of materials of construction are used. In the first, both the inner and outer walls are of low temperature steel. In the second, the inner wall is of low temperature steel and the outer one is of pre-stressed concrete. In the third, both walls are of pre-stressed concrete. In all three of these designs the outer wall also is capable of containing the cold liquid. The membrane tank consists of a pre-stressed concrete containment lined with a stainless steel membrane.

Details of the internals of an LNG storage tank are shown in Figure 22.14. The construction of LNG storage tanks is discussed by Steimer (1983).

22.11.2 Separation distances

Separation distances for LNG storage are given in NFPA 59A.

22.11.3 Secondary containment

Where the tank itself provides only single containment, secondary containment may be provided in the form of a bund. The bund height may be low, intermediate or high. Since the bund has to contain the full contents of the tank; a low bund has to be located at some distance from the tank; a high bund can be located close to the tank; and the intermediate height bund can be located at an intermediate distance from the tank. Such bunds may be used with a single wall tank or a double wall tank. A high concrete bund should not be confused with the outer pre-stressed concrete wall of a double integrity tank. The latter is not structurally independent of the tank, whereas the former is. A high bund may, however, appear to be part of the tank, since it may be very close to it and may have its own roof.

22.11.4 Foundations

Foundations for LNG tanks are of two main types. One is an elevated pilecap foundation, with free air circulation. The second is a ringwall foundation with a heating system. An account is given by Steimer (1983).

The monitoring of the settlement of the foundations has been described by Morrison (1987).

22.11.5 Insulation

A typical insulation for a single wall tank is polyurethane with a metal jacket. For double wall tanks use is made of perlite between the two walls. Insulation materials used for the suspended deck include perlite, mineral wool and fibre glass.

22.11.6 Ancillary facilities

Ancillary facilities for refrigerated LNG tanks include the refrigeration system and the pumping facilities. Accounts are given by Collins *et al.* (1983), Gilbert *et al.* (1985), Crawford, Durr and Handman (1986) and Morrison (1987).

An LNG storage is likely to be part of a terminal and vapour is generated from a number of sources, as described by Collins *et al.* Apart from those associated

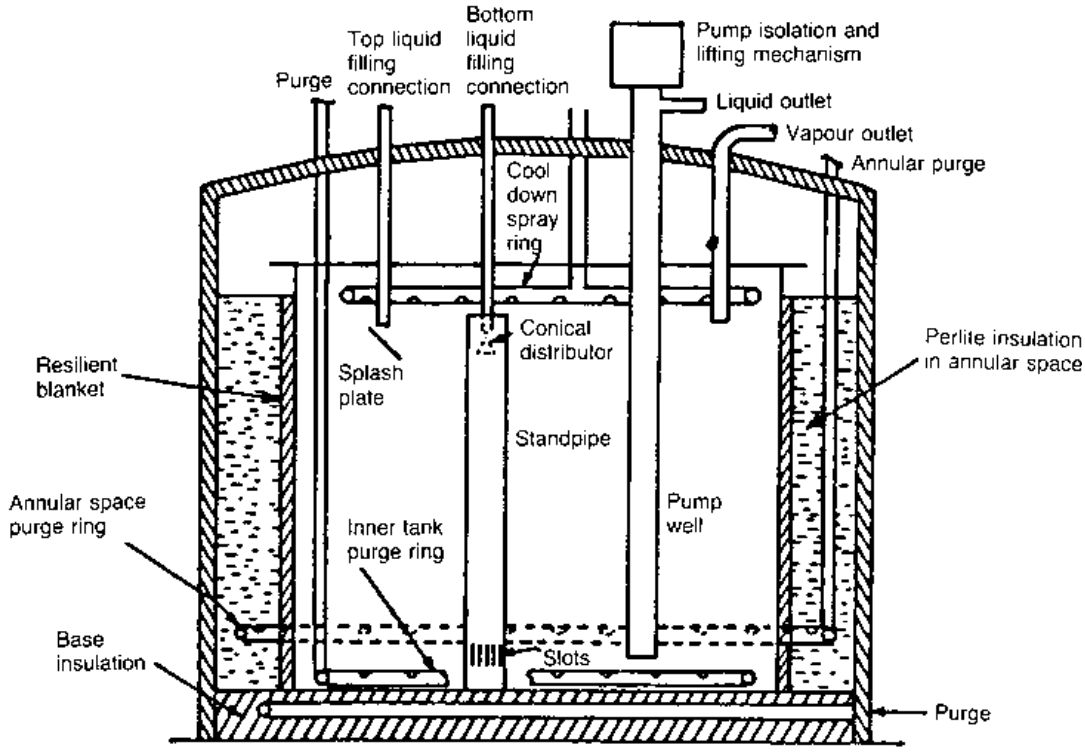


Figure 22.14 *LNG refrigerated storage tank internals (Crawford, Durr and Handman, 1986) (Courtesy of Gastech)*

with the tank itself, these sources include superheated liquid rundown from process units, heat in-leak into pipework and flash vapour formed during the loading of ships. The maximum vapour load may well occur during ship loading. Refrigeration facilities are provided to deal with these loads, but peak vapour flows are sent to the flare.

Pumping is required both for loading and for circulation, in order to prevent stratification. The tank system described by Morrison has six in-tank loading pumps and one circulation pump.

22.11.7 Instrumentation

A refrigerated LNG storage tank should be provided with suitable measurements of and alarms for the liquid level, the pressure and temperature in the tank and the boil-off gas flow.

Principal features of the instrumentation are the arrangements to prevent overpressure and overfilling. Pressure control is an integral part of the refrigeration system.

The monitoring of the movement of the inner tank has been described by Steimer (1983).

NFPA 59A requires that an LNG facility have an emergency shut-down system and gives details of the system to be provided.

22.11.8 Pressure relief

The tank also requires pressure relief and vent disposal arrangements. Accounts are given by Crawford, Durr and Handman (1986) and Morrison (1987).

Pressure rises may occur due to heat in-leak into the tank, high liquid in-flows, the in-flow of superheated liquid, vaporization due to pumped recirculation, a fall in barometric pressure, failure of the pressure control system, heat input during a fire, or rollover. Causes of vacuum include high liquid withdrawal flows, the in-flow of subcooled liquid, and a rise in barometric pressure.

Pressure relief is provided by pressure relief valves and vacuum protection by vacuum breaker valves. In the system described by Crawford, Durr and Handman (1986), the pressure relief valves vent to atmosphere and the vacuum breakers admit air.

The pressure control system may be arranged so that if the vapour flow is too great for the refrigeration system to handle, vapour is vented to the flare before opening of the pressure relief valves occurs. Operation of the vacuum breakers may be forestalled by vacuum control, which admits fuel gas.

22.11.9 Fire protection

Fire protection of refrigerated LNG storage tanks has much in common with that for other types of storage tanks for flammable products. Guidance is given in

NFPA 59A. Further accounts are those by Closner and Wesson (1983) and Morrison (1987).

NFPA 59A refers to the need for hazardous area classification, for flammable gas detection and to a range of fire control and extinguishing systems such as water sprinkler, foam and dry chemical systems.

Closner and Wesson describe a number of fire protection measures. These are: (1) containment systems which limit the size of the pool, and hence of any fire; (2) protective coating systems; (3) foam systems; and (4) water deluge systems.

The tank system described by Morrison is designed to withstand a collapse of the roof and the resultant tank fire. In these circumstances the outer wall would be subject to hydrostatic pressure and severe thermal gradients from the flame, which is assumed to be tilted.

22.11.10 Annular space

In a double wall tank some attention needs to be given to the annular space between the two tanks, and in particular to the entry of LNG into the space. One way in which this can occur is by condensation, caused by an increase in pressure in the tank. In some cases the annular space is purged with nitrogen.

Another situation is that which results from a leak of LNG from the inner tank. If this is sufficiently large, the formation of vapour may generate a pressure sufficient to rupture the inner tank. An account of this problem in a double wall ammonia tank and its solutions has been given by Squire (1991), as described in Section 22.18.

22.11.11 Inspection

There is relatively little published on the inspection of, and inspection intervals for, refrigerated LNG storage tanks. An account of the design of storage tank internals to facilitate the decommissioning and recommissioning of the tank has been given by Crawford, Durr and Handman (1986), who describe these operations in detail.

22.11.12 Rollover

Under certain conditions, 'rollover' of the liquid in an LNG tank can occur, resulting in the rapid evolution of a large quantity of vapour with the potential to over-pressure the tank.

Stratification can occur in an LNG tank if the density of the liquid 'cargo' charged to the tank is significantly different from that of the 'heel' already in the tank. As described above, there are in fact appreciable differences in density between LNGs from different sources.

A model of rollover in LNG tanks has been given by Germeles (1975b), who develops an earlier model by Chatterjee and Geist (1972). The liquid in the tank is assumed to be stratified into a number of 'cells' with heat in-leak from the sides and from the bottom of the tank as shown in Figure 22.15. The model consists essentially of the unsteady-state heat and mass balance equations for these cells and of supporting correlations.

The model draws on previous work by J.S. Turner (1965) on the mass and heat transfer between the interfaces of cells in stratified layers of saline solutions of different strength. He defines an interface stability parameter R

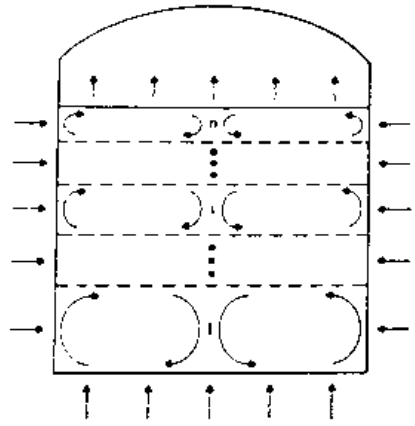


Figure 22.15 *An LNG storage tank with the liquid stratified into n cells (Germeles, 1975b) (Courtesy of the Plenum Publishing Corporation)*

$$R = \left|\frac{\beta\delta S}{\alpha\delta T}\right| \qquad [22.11.1]$$

where S is the concentration of the solute (mass fraction), T is the absolute temperature (K), α is the coefficient of expansion with respect to the temperature, T and β is the coefficient of expansion with respect to the concentration. The heat and mass transfer coefficients are given as functions f_1 and f_2 of R.

Another relation used in the Germeles model is the boil-off model by Hashemi and Wesson (1971). The boil-off rate b is given by

$$b = 0.328\frac{\rho_o C_p}{H_v}\frac{(g\alpha k^2)^{\frac{1}{5}}}{\rho\mu C_p^2}(T_n - T_s)^{\frac{4}{3}} \qquad [22.11.2]$$

where b is the boil-off mass flux, C_p is the specific heat of the liquid, g is the acceleration due to gravity, H_v is the latent heat of vaporization of methane, k is the thermal conductivity of the liquid, T_n is the absolute temperature of the top or nth cell, T_s is the absolute saturation temperature of methane in LNG, μ is the viscosity of the liquid, ρ is the density of the liquid and ρ_o is the average reference density of the liquid.

In the Germeles model, equilibration of the liquid densities is taken as the necessary and sufficient criterion for mixing. In this aspect his model differs from that of Chatterjee and Geist, which requires equilibration of both temperature and composition.

Some results from a simulation of the La Spezia rollover obtained by Germeles using his model are given in Figure 22.16. As Figure 22.16(a) shows, there is at rollover equilibration of density, but not necessarily of temperature or composition. Figure 22.16(b) shows the rapid increase in boil-off. The computed time to rollover is 34 hours, which compares with a time of 31 hours in the actual incident.

Further theoretical and experimental investigations of rollover in LNG tanks have been reported (e.g. Nakano *et al.*, 1983; Takao and Suzuki, 1983).

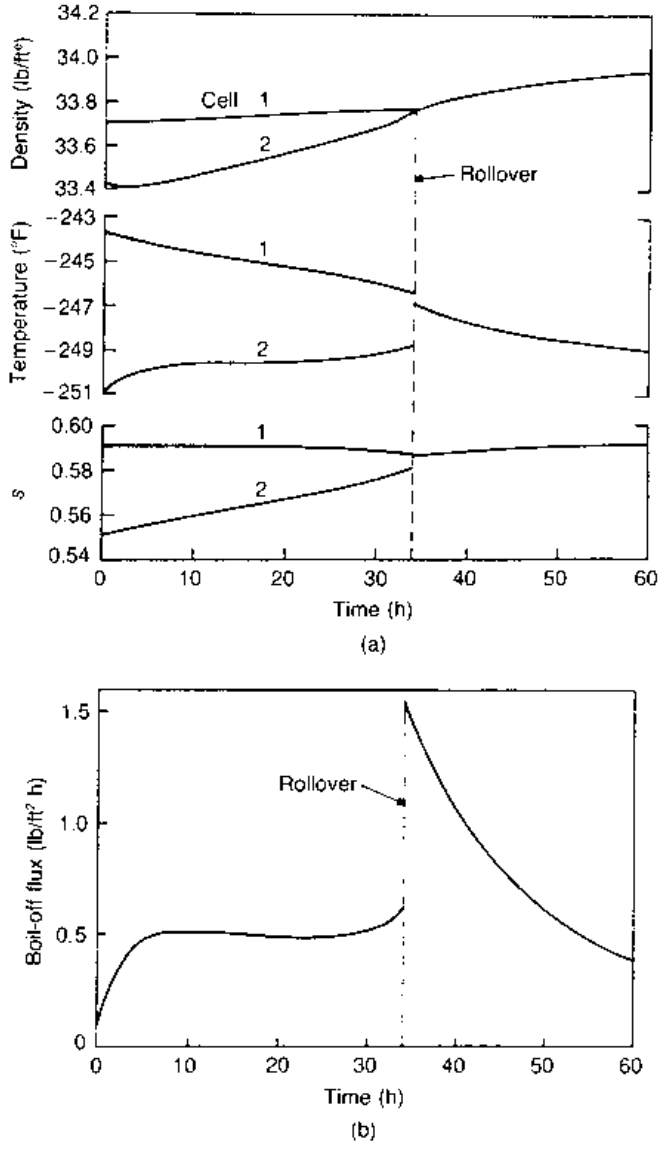


Figure 22.16 *Simulation of the rollover of LNG in the tank in the La Spezia incident (Germeles, 1975b): (a) density, temperature and impurity concentration S; (b) boil-off flux (Courtesy of the Plenum Publishing Corporation)*

There are a number of measures which can be taken to reduce the risk of rollover. Accounts of such measures are given by Chatterjee and Geist (1972) and by Drake, Geist and Smith (1973). They include:

(1) limitation of the variation in LNG composition;
(2) mixing of the tank contents by the use of top and bottom filling points;
(3) mixing of the tank contents by pump recirculation;
(4) pressure control of the tank;
(5) monitoring of parameters related to stratification;
(6) provision of a high capacity vent.

In some cases it may be possible to limit the variation of LNG composition, but in others this is not attractive. Mixing of the tank contents may be effected during filling by using top or bottom filling to charge a cargo which is more or less dense than the heel. Mixing during filling may be enhanced by jet mixing devices. Mixing during and after filling by recirculation pumps

may also be used, although this is a slow method and it may take too long; it also increases the heat inleak. Control of pressure in the tank may be used to give controlled evolution of vapour from the liquid. There are several parameters which may be used to monitor stratification. One is the liquid temperature profile in the tank. Another is the difference in density between the feed and the tank liquids, a third is the vaporization rate in the tank. Protection of the tank if rollover occurs despite these other measures requires the provision of a high capacity vent. The peak vapour evolution rate resulting from a rollover is difficult to estimate and the vent needs to be generously sized.

The rollover hazard receives mention in a number of accounts of LNG tank systems, including those by Collins *et al.* (1983), Crawford, Durr and Handman (1986) and LeChat and Caudron (1987).

22.11.13 Particular installations

There are a number of accounts of particular refrigerated atmospheric storage installations for LNG.

The Montoir de Bretagne LNG terminal is described by Lechat and Caudron (1987). They discuss the potential for rollover due to differences in the composition of the LNG cargoes received, and the precautions taken.

An account of the LPG and LNG terminal at Das Island is given by Morrison (1987). He describes in detail the tanks, foundations, ancillary equipment, pressure relief and fire protection.

22.11.14 Storage vessels

Although an atmospheric storage tank is the norm for refrigerated land-based LNG storage, a pressure vessel may also be used, as described by Itoyama *et al.* (1989). The vessel is essentially an adaptation of the MRV storage sphere used on LNG carriers. It has an inner shell of aluminium, to ensure strength at a cryogenic condition, and an outer shell of mild steel.

22.11.15 Underground storage

A number of early LNG storages took the form of an earth pit. The ground around the pit was frozen by the cold liquid, thus providing a seal. One such installation was the 21 000 te LNG storage at the British Gas terminal at Canvey.

Experience with such earth pit storages, described by Ferguson (1975), was not good. Problems were experienced in making the containment leak-tight and waterproof and with fissuring of the ground. The heat inleak resulted in a boil-off rate which was uneconomic. Thus, whereas the boil-off for a good above-ground tank is of the order of 0.04% per day by volume, that for an earth pit storage is some 0.1–0.3%.

The abandonment of earth pit storage at Canvey meant that of some dozen such storages, by 1975 only one remained in use. However, the concept of underground storage remains alive. Conceptual designs for cavity storage of LPG and LNG have been described by Lagron, Boulanger and Luyten (1986).

22.11.16 Mounded storage

More success has been achieved with mounded storage in which the LNG pressure vessel is set in an earth mound. This method has already been described in relation to LPG storage.

The method has been used in Japan, as described by Collins *et al.* (1983). In some cases use has been made of a concrete tank with its roof at grade, whilst in others the tank has been constructed at ground level and surrounded by a full earth berm.

22.12 Hydrogen Storage

Hydrogen is stored both as a gas and as a liquid. Relevant codes are NFPA 50A: 1989 *Gaseous Hydrogen Systems at Consumer Sites* and NFPA 50B: 1989 *Liquefied Hydrogen Systems at Consumer Sites.* Also relevant are *The Safe Storage of Gaseous Hydrogen in Seamless Cylinders and Containers* (BCGA, 1986 CP 8) and *Hydrogen* (CGA, 1974 G-5). Accounts are also given by Scharle (1965) and Angus (1984).

The principal type of storage for gaseous hydrogen is some form of pressure container, which includes cylinders. Hydrogen is also stored in small gasholders, but large ones are not favoured for safety reasons. Another form of storage is in salt caverns, where storage is effected by brine displacement. One such storage holds 500 te of hydrogen.

A typical industrial cylinder has a volume of 49 l and contains some 0.65 kg of hydrogen at 164 bar pressure. The energy of compression which would be released by a catastrophic rupture is of the order of 4 MJ. There is a tendency to prohibit the use of such cylinders indoors.

Liquid hydrogen is stored in pressure containers. Dewar vessel storage is well developed with vessels exceeding 12 m diameter.

NFPA 50A requires that gaseous hydrogen be stored in pressure containers. The storage should be above ground. The storage options, in order of preference, are in the open, in a separate building, in a building with a special room, and in a building without such a room. The code gives the maximum quantities which should be stored in each type of location and the minimum separation distances for storage in the open.

For liquid hydrogen NFPA 50B requires that storage be in pressure containers. The order of the storage options is the same as for gaseous hydrogen. The code gives the maximum quantities which should be stored in each type of location and the minimum separation distances for storage in the open.

Where there are flammable liquids in the vicinity of the hydrogen storage, whether gas or liquid, there should be arrangements to prevent a flammable liquid spillage from running into the area under the hydrogen storage. Gaseous hydrogen storage should be located on ground higher than the flammable storage or protected by diversion walls.

In designing a diversion wall the danger should be borne in mind that too high a barrier may create a confined space in which a hydrogen leak could accumulate. Scharle (1965) draws attention to the risk of detonation of hydrogen when confined and describes an installation in which existing protective walls were actually removed for this reason.

Pressure relief should be designed so that the discharge does not impinge on equipment. Relief for gaseous hydrogen should be arranged to discharge upwards and unobstructed to the open air.

Hydrogen flames are practically invisible and may be detected only by the heat radiated. This constitutes an additional and unusual hazard to personnel which needs to be borne in mind in designing an installation.

22.13 Toxics Storage

The topic of storage has tended to be dominated by flammables. It would be an exaggeration to say that the storage of toxics has been neglected, since there has for a long time been a good deal of information available on storage of ammonia, chlorine and other toxic materials. Nevertheless, the disaster at Bhopal has raised the profile of the storage of toxics, especially in respect of highly toxic substances.

In the USA, in particular, there is a growing volume of legislation, as described in Chapter 3, for the control of toxic substances. Attention centres particularly on high toxic hazard materials (HTHMs).

Some of the factors which need to be taken into account in relation to storage of HTHMs are now considered.

22.13.1 Inherent toxic hazard

The starting point is the characterization of the toxic hazard. The toxicity of the substance is one aspect of this. Another is the inventory. But the potential for harm also depends very much on features of the substance and its storage which determine its emission and dispersion.

There are a variety of toxic exposure limits which have been devised for different purposes such as the threshold limit value (TLV) and the emergency exposure limit (EEL), but these tend to be of limited use in assessing the toxic hazard. Various attempts have been made to devise more appropriate indices such as the Dow Chemical Exposure Index (CEP). These exposure limits and indices are described in Chapter 18.

The most realistic approach to the characterization of the inherent toxic hazard, however, would appear to be some form of hazard assessment, which need not necessarily amount to a full risk assessment, but may be limited to consequence assessment.

22.13.2 Inherently safer design

As for other process activities, so for HTHM storage the principle of inherently safer design should be applied. In the case of HTHM storage this means in particular examining the products made and the whole series of processes used to make them, whether at the assessor's site or elsewhere, with a view to the use of more benign chemicals and to the reduction of toxics inventories throughout the production and transport chains. In particular, it should be an aim to eliminate intermediate storage. Illustrations of the application of inherently safer design with regard to toxics, including toxics storage, are given in Chapter 11.

Another aspect of inherently safer design in storage is the storage conditions. The choice between pressure or refrigerated storage is the obvious example. But storage can be made inherently safer in other ways also, such as choosing the storage temperature such that it reduces the load on the disposal system should it become necessary to depressurize.

22.13.3 Storage siting and layout

Storage for HTHMs should be sited so as to minimize the frequency and the consequences of any release. The consequences of a release may be reduced by the provision of separation distances between the storage and potential targets, exploitation of the terrain and provision of escape routes. Measures to reduce frequency include segregation from flammables, minimization of interactions with transport terminals and minimization of domino effects.

22.13.4 High integrity design

Plant used for the storage of HTHMs should be high integrity plant. The high integrity design features should cover, among other things, (1) plant layout, (2) vessels and tanks, (3) pipework, (4) loading and unloading facilities, (5) secondary containment, (6) instrumentation, (7) pressure relief and disposal systems, and (8) contaminant control.

For the most part the codes and standards which govern plant design are oriented to flammables rather than toxics. There is relatively little guidance on toxics specifically.

The American Society of Mechanical Engineers (ASME) *Boiler and Pressure Vessel Code* does, however, recognize a category of 'lethal service', where the gases or liquids contained are of lethal toxicity. The ASME main piping code B31.3 has a Category M which is of similar purport.

The plant layout for HTHMs should include arrangements for the containment of liquid spillages by the use of bunds or other measures.

Pressure vessels and atmospheric tanks for HTHM storage should be built to high integrity standards. It is not usual to use double integrity tanks for HTHMs, though they are used for ammonia. But other measures to enhance integrity such as full radiography of welds, stress relieving and so on, should be used. Foundations and supports should also be of high integrity.

Likewise, pipework and fittings and equipment such as pumps should be to high integrity standards. Special attention should be paid to potential weak points such as nozzles, welds, flanges, gaskets and pipe supports. Events which might cause failure of pipework or equipment, such as hammerblow or vibration in the pipe or deadheading or cavitation in pumps, should be given extra consideration.

There are two quite separate aspects to pipework integrity. The measures just described are aimed at the prevention of serious failures. It is also necessary to aim for a high degree of leak-tightness in order to prevent fugitive emissions.

The disposition of the pipework into and out of the storage is another relevant feature. Lines connected below the liquid surface are a major source of large leaks and are to be avoided.

Provision needs to be made to shut off or reduce leaks which may occur in the form of excess flow valves, remotely operated isolation valves, and so on.

Extra consideration should be given to external threats to the containment, whether due to impacts such as dropped loads or vehicles or to natural events.

Associated with storage are loading and unloading facilities which are another potential source of release. Features of such facilities which are not present in

storage itself and which tend to increase the risk include: (1) a higher level of activity; (2) the involvement of personnel from different companies; (3) connections which are constantly made and unmade and which may be relatively fragile; (4) the movement of vehicles, including moving off whilst still connected; (5) the absence of secondary containment. The design should aim to minimize these problems.

The provision of secondary containment should be considered. Types of secondary containment include double integrity containments, double-walled pipes, dump tanks, bunds, drainage and sump systems and enclosures.

Some part of the instrument and control systems for HTHM storage may need to be high integrity. At the very least good practice should be followed in matters such as the use in critical applications of a sensor separate from that of the control loop for an alarm or a trip. It may be necessary in some cases to consider high reliability instrument systems based on the use of redundancy.

Systems for pressure relief on HTHM storage should receive extra attention. The relief and disposal system appropriate depends on the nature and quantity of fluid to be handled. Whatever system is selected, it too should be of high integrity.

A storage can be put at risk by the entry of a contaminant which either itself reacts with the material stored or catalyses a reaction. For some chemicals it is necessary to include in the design features that prevent such contamination.

22.13.5 High integrity operation

High integrity in the design needs to be complemented by high integrity in the operation of the plant. It is not appropriate to rehearse here the various features of good practice in operation and maintenance, but a few salient points can be made.

Storage is not simply a passive adjunct to the main process plant. It too is actively operated by filling and emptying. These operations have the potential to cause destructive overpressure or underpressure and to cause overfilling, and they need to be carefully controlled.

The storage should be operated so as to exclude contaminants which might cause reaction of the material held. Likewise, operations should not result in serious depletion of any necessary stabilizer.

Where the HTHM is flammable as well as toxic, measures should be taken to control ignition sources, including procedures to prevent ignition by static electricity.

Activities in the vicinity of storage, such as lifting of loads or movement of vehicles, should be controlled so that they do not pose an impact threat.

Storage systems tend to have a quite large proportion of items for use only in an emergency and which tend to be neglected and are often found to be either in poor condition or in the wrong state. Examples are blocked pipes or closed valves on water spray systems or open valves on water drainage lines through bunds.

With regard to maintenance, some aspects of particular importance in HTHM storage include (1) the identification and ranking of critical features, (2) inspection to detect unrevealed failures, (3) preventive maintenance, (4) isolation procedures and (5) documentation.

Table 22.10 *Some principal topics in the CCPS* High Toxic Hazard Material Storage Guidelines *and their treatment in this text*

		Chapter No.
1.	Overview	
2.	Risk assessment	9
3.	Plant design	
	3.1 Inherently safer design	11
	3.2 Plant siting	10
	3.3 Plant layout	10
4.	Design of storage and piping	12, 22
5.	Loading and unloading facilities	22, 25
6.	Instrumentation and control	13
7.	Isolation and containment	12, 22
8.	Inspection and maintenance	19, 21
9.	Operating procedures and training	14, 20, 28
10.	Emergency planning	24

The operating discipline should ensure that all protective features are maintained in operational condition, whether these be heating or cooling systems, instrumented protective systems, relief systems or fire protection systems.

22.14 High Toxic Hazard Materials: CCPS *Guidelines*

The Center for Chemical Process Safety (CCPS) has published guidance on the storage of high toxic hazard materials, and this is now described.

22.14.1 CCPS *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials*

The CCPS *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials* (1988/3) (the CCPS *HTHM Storage Guidelines*) cover a wide range of topics on HTHM storage. Many of these topics are dealt with in other parts of the present text. Table 22.10 gives an indication of the chapters or sections in which these topics are treated.

22.15 Chlorine Storage

Storage of chlorine as a liquid is mainly either at chemical works or at installations where it is required for water treatment such as waterworks, power stations and swimming baths. Its boiling point is -34°C.

Guidance on the handling and storage of chlorine is given in HS(G) 28 *Safety Advice for Bulk Chlorine Installations* (HSE, 1986). This guidance is based on the earlier *Guidelines for Bulk Handling of Chlorine at Consumer Installations* (CIA, 1980/14) (the CIA *Chlorine Storage Guide*), which itself followed *Code of Practice for Chemicals with Major Hazards: Chlorine* (BCISC, 1975/1) (the CIA *Chlorine Code*). HS(G) 28 is the guidance now listed by the Chemical Industries Association (CIA).

Further guidance is given in the various publications of the Chlorine Institute, including *Chlorine Manual* (1986, Pmphlt 1), *Non-refrigerated Liquid Chlorine Storage* (1982, Pmphlt 5), *Refrigerated Liquid Chlorine Storage* (1984, Pmphlt 78), *Piping Systems for Dry Chlorine* (1985,

Pmphlt 6), *Operation of Chlorine Vaporizing Equipment* (1979, Pmphlt 9) and *Chlorine Tank Car Loading, Unloading, Air Padding, Hydrostatic Testing* (1979 Pmphlt 66).

The account given here is confined to chlorine storage. Chlorine itself is discussed in Chapter 11, pipework for chlorine systems is discussed in Chapter 12 and chlorine unloading facilities are described in Section 22.26.

22.15.1 Regulatory requirements

The storage of chlorine is governed by the NIHHS Regulations 1982 and the CIMAH Regulations 1984. The NIHHS notifiable inventory is 10 te. The CIMAH inventory for which demonstration of safe operation may be required (Regulation 4) is 10 te and that which attracts a safety case (Regulation 7) is 75 te.

22.15.2 Storage conditions

Chlorine is generally stored under pressure at atmospheric temperature, but may also be stored fully refrigerated at -34°C and atmospheric pressure.

22.15.3 Storage systems

Chlorine should be stored in bulk only if it is used in quantities which make the use of drums impractical. A chlorine storage vessel should have a capacity appreciably greater than a full load from a road tanker or rail tank car. It is preferable to keep the number of vessels to a minimum in order to avoid complexity and proliferation of potential leak sources, but flexibility and continuity of supply require at least two vessels.

The *Chlorine Code* gives a well defined philosophy for the storage of chlorine. In view of the importance of the hazard of toxic release from storage, the *Code*'s statement of the problem is of interest:

> Liquid stored in bulk is the potential source of the most serious incidents.
>
> Stored liquid could be released:
> (1) By failure of the vessel holding it.
> (2) By failure of pipework or equipment connected to that vessel.
> Stocks necessarily carried to conduct normal operation in the businesses are such that the techniques of design and operation of any storage must eliminate the risk of complete vessel failure leading to release of its contents.
> (1) Liquefied gas storage can be designed, fabricated, inspected and maintained so that there is no possibility of a tank releasing its contents while it is kept within design conditions.
> (2) Protective systems of quantified high reliability and availability can be designed to ensure that these physical conditions are maintained.
> (3) Impurities can be controlled to obviate abnormal corrosion.
> (4) These measures may be backed up by relief systems such that the combination of vessel design, protection, quality control and relief eliminates the possibility of complete vessel failure.
> (5) Liquefied gas storages can be sited, or given protective barriers, such that they are fully protected from external damage other than civil commotion, sabotage, act of war, or falling aircraft.

From these first premises it follows that, although the risk of some damage to a storage vessel cannot be totally eliminated, the main dangers derive from failure of pipework or equipment whether on producing or using plants or connected to storage.

The critical factors in preventing escapes are:
(1) Arrangements for isolation of stocks from all other equipment.
(2) Arrangements for isolation of process vessels from all other equipment.
(3) Protection from external damage.
(4) Means of maintaining design conditions and relieving abnormal conditions.
(5) Means for disposal of purged or vented material.
(6) The effect of chemicals and conditions in using processes on the design and operating requirements.
(7) Means for the retention of spillages near the point of origin and for their treatment. The capacity of the retention area shall be sufficient for, but need not be more than, the largest spillage which can reasonably be envisaged. The walls of the retention area shall, however, be sufficiently high to contain also any material used in treating the spillage.

22.15.4 Materials of construction

Materials of construction for chlorine handling are discussed in Chapters 11 and 12, and are therefore not dealt with in detail here, but there are a few matters which merit mention at this point. The normal material of construction for chlorine storage vessels is mild steel. Mild steel is satisfactory for the handling of dry gaseous or liquid chlorine, but not of wet chlorine. There are, however, upper and lower temperature limits for mild steel in chlorine which should not be exceeded.

22.15.5 Storage vessels

Chlorine pressure storage vessels are usually horizontal cylindrical vessels for the smaller capacities and spherical vessels for the larger ones. Pressure storage spheres up to 400 te capacity have been used for chlorine, but some large vessels have been taken out of use, thus reducing the hazardous inventory.

A chlorine pressure storage vessel should be designed to BS 5500: 1991 Category 1 or equivalent, but with the additional requirements of HS(G) 28.

HS(G) 28 states that a chlorine storage vessel should have a minimum design pressure of 12 barg (174 psig). The minimum design temperature should be -35°C, the temperature to which liquid chlorine will drop if completely depressurized. The normal design range for temperature is -35°C to 45°C.

With regard to the filling ratio, there is no standard equivalent to BS 5355: 1976 for transportable liquid containers. HS(G) 28 states that for chlorine the figure normally used is 1.25 kg of liquid chlorine/litre of capacity, which ensures that even at 50°C the volumetric fill does not exceed 95%.

The connections on a chlorine storage vessel should be held to a minimum and kept simple. Connections required are (1) a liquid chlorine inlet, (2) a liquid chlorine outlet, (3) vent and padding air lines, (4) a relief system and (5) instrument connections. Lines entering below the liquid level are to be avoided so that any

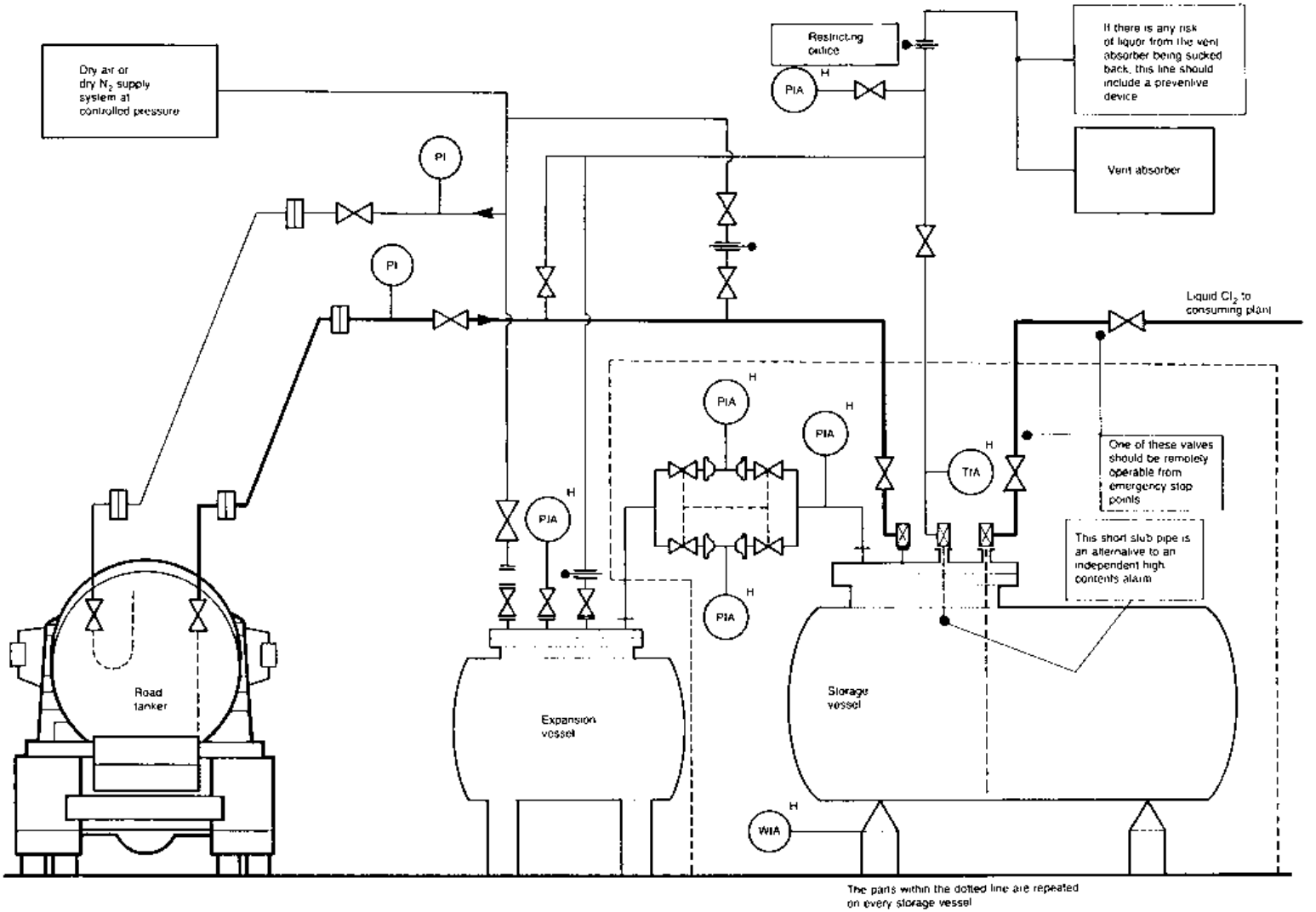


Figure 22.17 *General arrangement for a chlorine pressure storage installation and road loading facility (Health and Safety Executive, 1986 HS(G) 28) The original diagram contains cross-references to certain paragraphs in HS(G) 28. (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

release is of gas rather than of liquid. The preferred arrangement is that all the connections should be through a manhole located on the top of the vessel. Detailed design of these lines is described HS(G) 28.

The vent and padding air lines may have separate connections or may be through a single combined connection. The vent should go to the gas absorption system.

The arrangements given in HS(G) 28 for a chlorine storage vessel and the associated unloading facilities are shown in Figure 22.17.

Chlorine storage vessels should be located above ground and provided with a bund. The bund should be able to take the contents of the largest storage vessel with adequate freeboard. The ground under a storage vessel should be sloped to allow drainage into a sump. Provision should be made to remove rainwater over the bund wall rather than through it.

22.15.6 Ancillary facilities

Ancillary facilities required for chlorine storage include: an expansion vessel to take any chlorine vented in the event of overfilling; a gas absorption unit for the disposal of the vented material; equipment for the transfer of liquid chlorine from storage to consumer plants; and vaporization equipment to provide chlorine gas to consumer plants. These facilities are described below.

22.15.7 Instrumentation

A chlorine storage vessel should be provided with suitable measurements and alarms on liquid contents, pressure and temperature. The measurement of the liquid contents should preferably be by means of load cells or a weighbridge.

Protection against overfilling should receive particular attention. As already stated, the vessel itself should be larger than the road tankers and rail tank car containers which deliver to it. There should be a high contents alarm, and possibly an extra-high contents alarm. A low contents alarm may also be appropriate. An ullage pipe may be provided on the vent line with a low temperature or other alarm to warn of entry of liquid chlorine into the line.

The storage should be provided with a chlorine gas detector system.

22.15.8 Pressure relief

For a chlorine storage vessel, pressure relief should be provided as an ultimate safeguard. HS(G) 28 requires that the pressure relief arrangements be a double stream system with isolation valves on the upstream and downstream sides of each stream, so that one stream can be operational whilst the other is under maintenance. There should be a safeguard against the risk of the simultaneous isolation of both streams, either by means of a mechanical interlock on the isolation valves or of a procedure for locking the valve.

For each relief stream, the relief devices should be either two bursting discs arranged back to back or a bursting disc followed by a pressure relief valve. Either way, there should be a pressure gauge on the space between the two devices. A pressure relief valve alone should not be used, owing to the risk of corrosion.

A single stream system with locked open isolation valves is in common use, but the arrangements described are the preferred ones.

An expansion vessel should be provided to receive the relief. It should be designed to the same standard as the storage vessels and should have a capacity about 10% of that of the largest vessel. It should be capable of being vented manually to the disposal system and should have its own high pressure alarm.

22.15.9 Absorption system

There should be suitable arrangements for the absorption of any chlorine vented. In some systems it is possible to arrange for the chlorine to be absorbed on a user plant, but normally a dedicated gas absorption system is required. As shown in Figure 22.17, the gas absorption system receives chlorine gas from normal venting and, via the expansion vessel, gas from the relief system.

The gas absorption system should be instrumented to ensure that the circulation of liquid and the concentration of absorbent are correct and to measure the concentration of chlorine in the outlet gas stream.

22.15.10 Transfer arrangements

The transfer of liquid chlorine from a storage vessel to consumer plants may be effected by vapour pressure alone, by padding gas pressure or by pumping. The first two methods are the most common.

The padding gas may be nitrogen or compressed dry air. Nitrogen for padding may be obtained from a liquid nitrogen vaporization unit. Compressed air should be dry to a dewpoint below −40°C and should be oil free. The padding gas should be held in a receiver with an operating pressure and with protective devices and instrumentation such that the storage cannot be overpressured by the padding gas. Detailed arrangements are described in HS(G) 28.

For pumping, which may be utilized where a higher pressure is required or where the padding gas cannot be tolerated, use is made both of submerged pumps installed inside the tank and of external pumps. For the latter a special pumping system has been developed in which the liquid chlorine is first transferred from the storage vessel to a separate pumping vessel and then fed to the pumps.

22.15.11 Vaporizers

Where chlorine is required in vapour form, a limited supply may be obtained from cylinders or drums, but the supply of any appreciable quantity requires vaporization facilities. It is not good practice to draw the gas from the vapour space of a chlorine storage vessel, as this creates the risks that process liquid may be drawn into the vessel and that less volatile impurities such as nitrogen trichloride may become concentrated.

HSE guidance on chlorine vaporizers is given in CS 16 *Chlorine Vaporizers* (1985) and HS(G) 28.

Three heating media are in use in chlorine vaporizers: hot water, steam and heat transfer fluids. The most common method is the use of hot water at about 60–70°C. Where steam is used it should be saturated and pressure limited to prevent overheating.

Four main types of vaporizer are used, as shown in Figure 22.18. Type 1 has some form of vertical tube

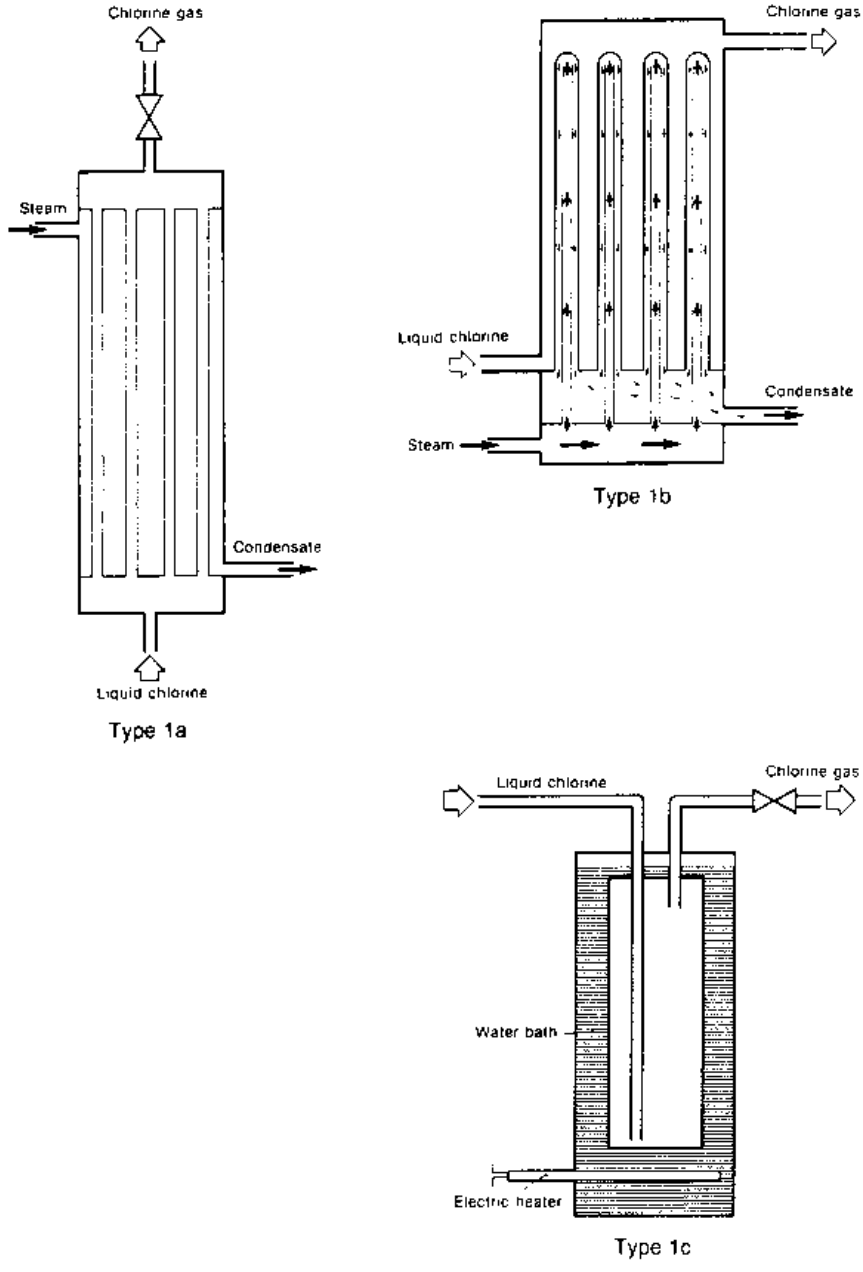
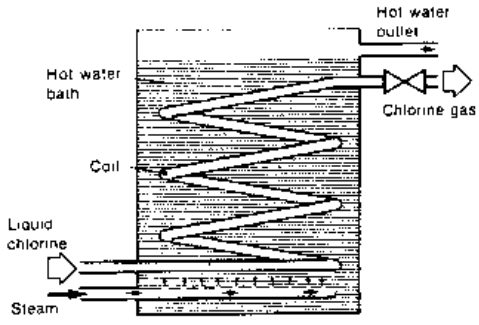


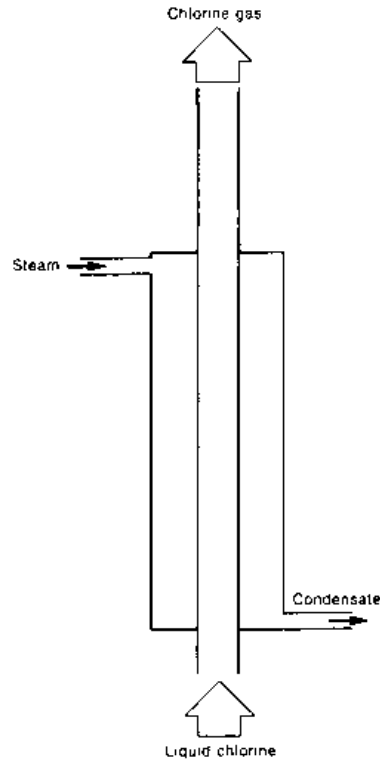
Figure 22.18 *Some types of chlorine vaporizer (Health and Safety Executive, 1986 HS(G) 28): (1a) shell and tube; (1b) steam bayonet; (1c) hot water bath; (2) coil tube immersed in heating bath; (3) concentric tube unit; and (4) kettle type evaporator (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

bundle, Type 2 is a coiled tube immersed in a heating bath, Type 3 is a concentric tube, or jacketed pipe, unit and Type 4 is a kettle, reboiler unit. HS(G) 28 discusses the characteristics of the different designs.

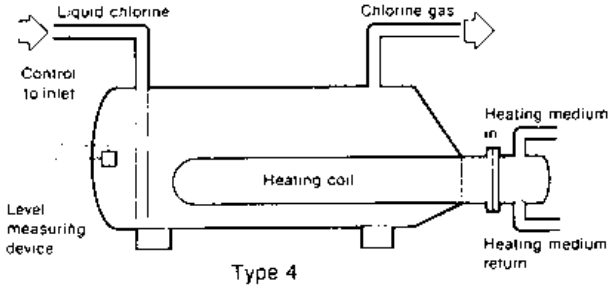
There are a number of potential problems and hazards associated with vaporizers. One is overpressurization. A vaporizer commonly operates at 70°C, at which temperature the vapour pressure of chlorine is some 21 bar. This



Type 2



Type 3



Type 4

Figure 22.18 *continued*

pressure can be realized in the vaporizer if it is isolated whilst containing the hot liquid. It is not usual in the UK to fit a pressure relief valve to a vaporizer.

Overheating can result in more rapid corrosion and, in the extreme, the combustion reaction between steel and chlorine. A temperature limit of 120°C is normally

observed. The pressure of steam used for heating is limited to 1 barg (15 psig), corresponding to a temperature of 120°C, with the steam saturated rather than superheated.

If the flow to the vaporizer is excessive, the heating is insufficient or the heat transfer surfaces are fouled, the chlorine vapour may lose superheat, liquid droplets may be entrained or the vaporizer may flood. It is even possible that ice may form on the heating surfaces. An indication of these problems may be obtained from the gas flow and temperature from the vaporizer. HS(G) 28 gives details of the controls required. A knockout pot may also be installed to remove liquid droplets.

If the chlorine becomes contaminated by water, whether by a pinhole leak of water or steam heating medium, or otherwise, rapid corrosion of mild steel can result. If vaporization of chlorine is partial rather than total, a concentration of impurities, notably nitrogen trichloride, can occur with the attendant risk of explosion.

Concentration of less volatile impurities such as nitrogen trichloride must be avoided. In some cases the vaporizer itself is designed to ensure that the nitrogen trichloride is vaporized together with the chlorine. Otherwise a separate purge and vaporizer circuit may be required to deal with the impurity residues.

Reverse flow of a process fluid into the vaporizer may occur if the pressure at the vaporizer falls or the process pressure rises or if the chlorine vapour condenses, creating a vacuum and causing suck-back.

Precautions need to be taken against these various hazards. Detailed measures are described in HS(G) 28.

22.15.12 Inspection

HS(G) 28 requires that an initial inspection be made when the vessel is brought into service and that there should be a first thorough in-service inspection within 5 years of commissioning. Thereafter the inspection interval should be determined by the inspecting authority, but should normally not exceed 5 years.

The guide gives details of the procedures to be followed in decommissioning and recommissioning the vessel and of the features to be inspected and the methods of inspection.

22.15.13 Storage operation

The principles governing the operation of chlorine storage are outlined in HS(G) 28.

22.15.14 Emergency arrangements

Emergency planning for chlorine storage is dealt with in HS(G) 28.

22.16 Ammonia Storage

Anhydrous ammonia is stored as a liquid, mainly either in chemical works or, particularly in the USA, in storage terminals supplying agricultural users. Its boiling point is −33°C.

The handling of ammonia, including its storage, has been a major preoccupation of the industry and this is reflected in the *Chemical Engineering Progress* series *Safety in Air and Ammonia Plants* (AIChE 1960–69/17–26) and *Ammonia Plant Safety (and Related Facilities)* (AIChE 1970–1994/31–52). The work of the industry storage committee has been described by Ball (1968b).

Guidance on ammonia storage is given in HS(G) 30 *Storage of Anhydrous Ammonia under Pressure in the United Kingdom* (HSE, 1986). Two CIA codes, *Code of Practice for the Storage of Anhydrous Ammonia under Pressure in the United Kingdom* (1975/13) (the CIA *Pressure Storage Code*) and *Code of Practice for the Large Scale Storage of Fully Refrigerated Anhydrous Ammonia in the United Kingdom* (1975/8) (the CIA *Refrigerated Ammonia Storage Code*), are no longer listed. A relevant US code is ANSI K61.1: 1989 *Safety Requirements for the Storage and Handling of Anhydrous Ammonia*.

The account given here is confined to ammonia storage. Ammonia itself is discussed in Chapter 11, pipework for ammonia systems in Chapter 12 and ammonia loading and unloading facilities in Section 22.26.

22.16.1 Regulatory requirements

The storage of anhydrous ammonia is governed by the NIHHS Regulations 1982 and the CIMAH Regulations 1984. The NIHHS notifiable inventory is 100 te. The CIMAH inventory for which demonstration of safe operation may be required (Regulation 4) is 50 te and that which attracts a safety case (Regulation 7) is 500 te.

22.16.2 Storage conditions

Ammonia is generally stored either under pressure at atmospheric temperature or fully refrigerated at −33°C and atmospheric pressure. A review of storage conditions has been given by C.C. Hale (1974).

22.16.3 Materials of construction

Materials of construction for ammonia handling are discussed in Chapters 11 and 12, and are therefore not dealt with in detail here, but there are a few matters which merit mention at this point. The normal material of construction for ammonia storage vessels and tanks is carbon steel. Ammonia reacts with copper and copper alloys, particularly if even traces of water are present, and they should not be used.

Materials of construction for ammonia handling need to be resistant to low temperatures and to stress corrosion cracking. High yield strength steels are more susceptible to stress corrosion cracking than lower yield strength steels, and an upper limit on strength may be specified. Austenitic steels are resistant to low temperature brittle fracture.

22.16.4 Storage statistics

Surveys of refrigerated ammonia storage with copious statistics have been given by C.C. Hale (1974, 1980, 1984) and C.C. Hale and Lichtenberg (1990). The following subjects are among those covered, though not every subject is dealt with in every survey: (1) number of tanks, (2) size of tanks, (3) types of tank, (4) total storage capacity, (5) location of storage (by state), (6) siting of storage, (7) fill sources, (8) operating temperatures and pressures, (9) foundations, (10) insulation, (11) secondary containment, (12) vapour recovery systems, compressors and condensers, (13) flare systems, (14) inert gas purge systems, (15) utilities, (16) manning, (17)

inspection, (18) downtime, (19) accident prevention programmes and (20) emergency planning.

22.16.5 Storage policies

As for LPG and LNG, so for ammonia, the last decade has seen a considerable evolution of storage policy. Some accounts of these changes are given by W.G. Jones *et al.* (1989), J.R. Thompson and Carnegie (1989) and Squire (1991).

J.R. Thompson and Carnegie (1989) describe the policy of Dupont to replace pressurized storage of ammonia with high integrity refrigerated atmospheric storage.

The policy of ICI is described by W.G. Jones *et al.* (1989). There the policy is to retain in use existing pressure storage spheres, but for new storage to use small stress relieved cylindrical vessels and refrigerated atmospheric tanks.

22.16.6 Storage operation

The principles governing the operation of ammonia storage are outlined in HS(G) 30 and in the CIA *Refrigerated Ammonia Storage Code.*

The point was made earlier that in many of its aspects storage is not a low technology activity. This is illustrated by the comment of Squire (1991) in an account of the measures taken to ensure the integrity of a particular large refrigerated ammonia storage tank: 'Most, if not all, of the personnel associated with the ammonia tank did not understand the "technology of the tank".'

22.16.7 Emergency arrangements

Emergency planning for ammonia storage is dealt with in HS(G) 30 for pressure storage and in the CIA *Refrigerated Ammonia Storage Code* and by C.C. Hale (1980). Hale describes an ammonia terminal emergency programme with emphasis on the properties and hazards of ammonia itself and on protective equipment for personnel.

22.17 Ammonia Storage: Pressure Storage

22.17.1 Storage vessels

Ammonia pressure storage vessels are usually horizontal cylindrical vessels for the small capacities and spherical vessels for the larger ones. It has been common practice to use pressure storage spheres with a capacity in the range 500 to 3000 te, but many spheres have suffered problems of stress corrosion cracking and some have been taken out of use.

An ammonia pressure storage vessel should be designed to BS 5500 Category 1, or equivalent, with due regard to Appendix D, which deals with low temperature steels, and taking into account the guidance given in HS(G) 30. HS(G) 30 gives separate treatments for cylindrical and spherical vessels, and this distinction is followed here.

22.17.2 Spherical vessels

HS(G) 30 states that an ammonia pressure storage sphere should be designed to withstand the stresses imposed when the vessel is full and the pressure in the vapour space is equal to the vapour pressure of ammonia at the maximum design temperature plus the partial pressure of any inert gases which may be present. The minimum design temperature should preferably be $-33^{\circ}C$, which is the temperature to which liquid ammonia will drop if completely depressurized, but in any event should not be greater than $-10^{\circ}C$.

The design should be such as to minimize the risk from stress corrosion cracking. The steel used should be not a high yield strength steel but one with a yield strength not exceeding 350 N/mm^2. The vessel should be fully stress relieved. These requirements apply to the design of a new vessel and are not necessarily met in existing vessels.

The inspection requirements given in HS(G) 30 include 100% magnetic particle inspection of all internal welds.

22.17.3 Secondary containment

It has been traditional to put bunds around all types of ammonia storage. But this practice has been questioned, for example by J.D. Reed (1974), in relation to pressure storage on the grounds that in this case sudden loss of containment tends to result in ejection of all the contents in the form of vapour, or spray, leaving no residual liquid.

HS(G) 30 recognizes this argument, but requires that an ammonia storage sphere should be provided with a bund. The bund should be able to take 20% of the capacity of the sphere, should be positioned outside the sphere radius and should be not less than 1 m high. The ground under the vessel should be sloped to allow drainage into a sump.

22.17.4 Ancillary facilities

The ancillary facilities required for ammonia storage include, in particular, pumps for the transfer of liquid ammonia from storage.

22.17.5 Instrumentation

An ammonia storage sphere should be provided with suitable measurements and alarms on liquid level, pressure and temperature. For level there should be at least two independent indicators. There should be a high level alarm independent of any indicators.

22.17.6 Pressure relief

HS(G) 30 requires that pressure relief on an ammonia storage sphere should be provided by means of at least two pressure relief valves. In addition, unless the sphere is designed for full vacuum, it should be protected by a vacuum break valve. Use may be made of separate pressure and vacuum valves or of the combined pressure/vacuum type.

There should be an isolation valve between each relief valve and the sphere, and a system should be incorporated to ensure that at any one time only one relief valve can be isolated.

22.17.7 Inspection

HS(G) 30 requires that an initial inspection be made when the sphere is brought into service and that there should be a first in-service inspection within 2 years of commissioning. A principal purpose of the inspection should be to detect any stress corrosion cracking which may have occurred, as described below. Provided the

results of inspection are satisfactory, the inspection interval may be increased in steps of 2 years up to a maximum interval of not more than 6 years.

The guide gives details of the procedures to be followed in decommissioning and recommissioning the vessel and of the features to be inspected and the methods of inspection.

22.17.8 Stress corrosion cracking

Much of the treatment of operation and inspection in HS(G) 30 is concerned with stress corrosion cracking. This problem is considered at more length in Section 22.19, but the recommendations of the guide may be noted at this point. These are to the effect that the oxygen content of the liquid ammonia should not exceed 2.5 ppm when the water content is as low as 100 ppm, and that serious consideration should be given to maintaining the water content at 0.2% w/w.

22.17.9 Cylindrical vessels

As mentioned above, HS(G) 30 gives a separate treatment for cylindrical pressure vessels for ammonia storage. The guide states that an ammonia pressure storage cylinder should be designed for a pressure of at least 15.5 bara. The design temperatures given are essentially as for a storage sphere. The arrangements given in HS(G) 30 for a ammonia storage cylinder and the associated unloading facilities are shown in Figure 22.19. For a storage cylinder, the guide does not require a bund, but there should be protection against vehicle impact.

The inspection requirements given in HS(G) 30 include 100% radiography of all butt welds, and ultrasonic and/or magnetic particle inspection of all other welds.

22.17.10 Semi-refrigerated vessels

It is convenient to deal here with pressure vessels for the semi-refrigerated, or semi-pressure, storage of ammonia. These are normally pressure spheres and are treated in HS(G) 30 together with pressure spheres for storage at atmospheric temperature. Principal differences are that with semi-refrigerated storage it is necessary to allow for the heat gain and resultant boil-off by provision of suitable thermal insulation and refrigeration.

Insulation materials that may be used include foam glass and polyurethane foam. HS(G) 30 draws attention to the importance of a vapour barrier and to measures to prevent the integrity of the containment being impaired by the materials used in, or the attachment of, the insulation.

22.18 Ammonia Storage: Refrigerated Storage

22.18.1 Storage tanks

Refrigerated liquid ammonia is stored in atmospheric storage tanks. Accounts of such storage are given in the CIA *Refrigerated Ammonia Storage Code* and by Shah (1982), Blanken (1987), J.R. Thompson and Carnegie (1989) and Herbertsson (1992).

Tanks used for refrigerated ammonia have developed from conventional atmospheric storage tanks. The design of atmospheric storage tanks in general is governed by API Std 620: 1990 *Design and Construction of Large, Welded, Low-pressure Storage Tanks* and API Std 650: 1988 *Welded Steel Tanks for Oil Storage*. For refrigerated ammonia storage frequent reference is made to API Std 650, Appendix R.

There are now in use a number of tank systems similar to those used for LNG. The single wall tank has a wall made of low temperature steel with external insulation covered by a vapour barrier. A double wall tank has an inner wall of low temperature steel and an outer wall of carbon steel with insulation in between. The outer wall is not designed to withstand the cold liquid, so this is still only a single containment system. A double integrity tank system has an inner tank with a suspended deck and an outer wall. Both the inner and outer walls are of low temperature steel. Accounts of tank systems make little reference to the use of prestressed concrete for either the inner or outer wall or of membrane systems.

22.18.2 Foundations

The foundations of refrigerated ammonia storage tanks require be protected against 'frost heave'. The problem and its prevention have been discussed by Morrison and Marshall (1970). Two principal types of foundation are used. One involves a tank bottom slab on piling so that there is free air circulation. In the other, the bottom slab is provided with insulation and electrical heating.

Further descriptions of foundation systems are given in the CIA *Refrigerated Ammonia Storage Code* and by C.C. Hale (1980) and C.C. Hale and Lichtenberg (1990).

22.18.3 Insulation

A refrigerated ammonia storage tank requires thermal insulation. The type of insulation which is suitable depends on the tank system. Principal types of insulation for single wall tanks are foam glass, polyurethane foam, reflective multi-layered aluminium and Styrofoam. For doubled wall tanks use is made of perlite insulation. The suspended deck used in double wall tanks counts as another form of insulation.

Insulation failures on single wall tanks are not unusual. A common cause is the penetration of moisture. Insulation problems have been described by a number of authors, including Hoffman (1967) and C.C. Hale (1974, 1980). Loss of a section of lagging is undesirable, because it allows rapid heat leak into the tank with a consequent increase in vaporization; it may also cause 'bump boiling'.

Reviews of the failure rates of insulation systems have been made by C.C. Hale (1974, 1980). He found that double wall tank systems filled with expanded perlite and reflective multi-layer aluminium systems had a good record compared with foam glass, polyurethane foam and Styrofoam systems.

Further descriptions of insulation systems are given by C.C. Hale (1984) and C.C. Hale and Lichtenberg (1990).

Squire (1991) has discussed the effect of insulation in a double integrity tank system in the event of a leak from the inner tank into the annular space. Tests showed that as the ammonia vaporized, the perlite insulation behaved like a spouted bed, resulting in a pressure of 55–69 kPA (8–10 psi). Solutions were to vent to annular space or install block Styrofoam insulation. No satisfactory way was found of doing the former, and for the tank in question the latter solution was adopted.

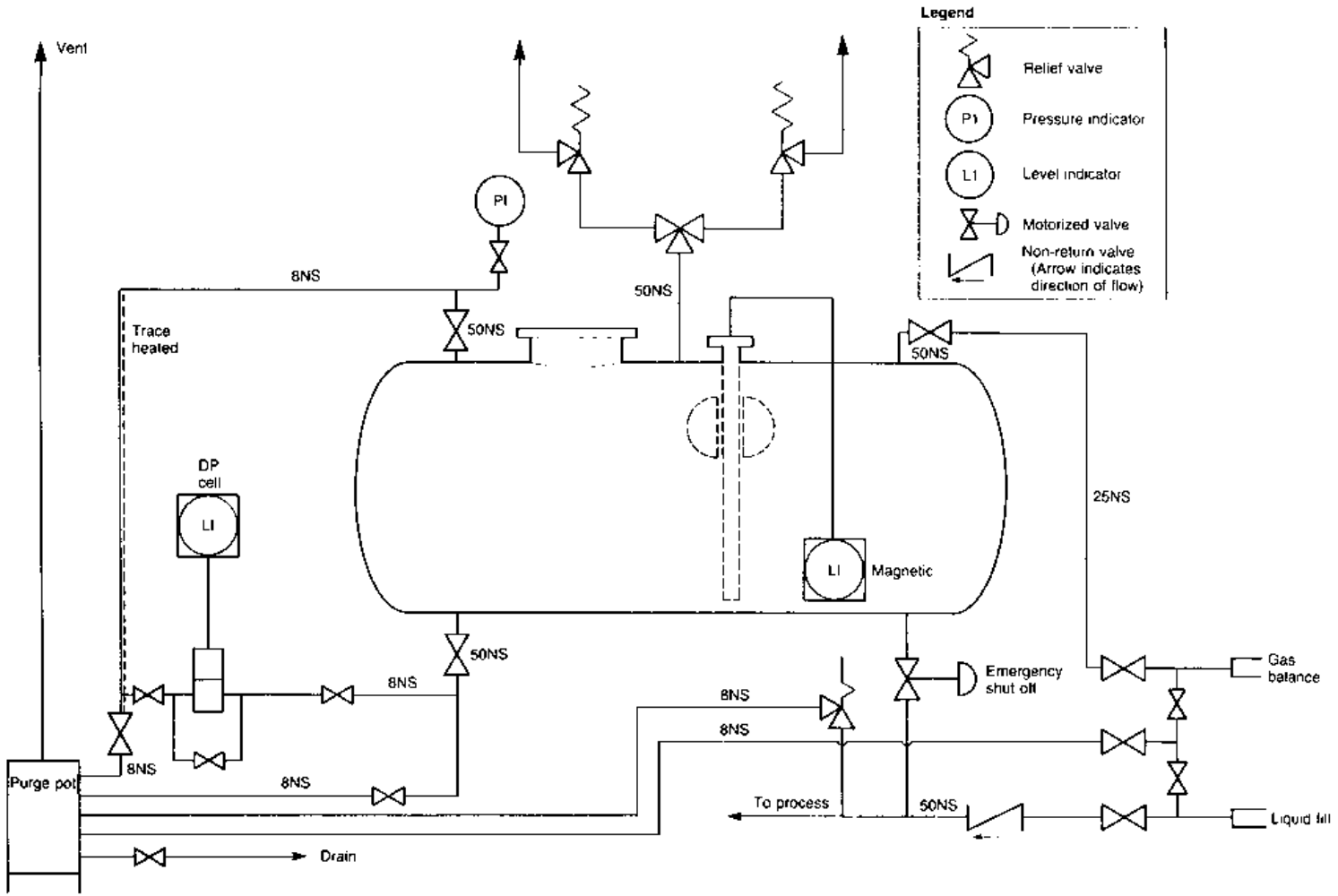


Figure 22.19 *General arrangement for an ammonia pressure storage installation (Health and Safety Executive, 1986 HS(G) 30) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

22.18.4 Secondary containment

Refrigerated ammonia storage tanks may be provided with some form of secondary containment. Accounts are given by Comeau (1972), MacArthur (1972), C.C. Hale (1974, 1980), J.D. Reed (1974), Hendriks (1980), Shah (1982), Blanken (1987) and C.C. Hale and Lichtenberg (1990).

Escape from refrigerated ammonia storage results in immediate flashing of only about 2% of the liquid. Even a primitive secondary containment should hold some 90% of the liquid.

Bunds and other measures to prevent dispersion of ammonia from refrigerated storage have been discussed by Comeau (1972). It is not necessarily enough simply to catch the liquid released. If a low bund with a large surface area is used, the large quantities of ammonia vapour vaporized from the liquid will still present a serious hazard. It is therefore desirable to reduce the surface area. There are various methods of doing this. Use may be made of controlled drainage which runs the liquid off to a pit where its evaporation is reduced. Foam blanketing is another possibility, provided the area to be covered is not excessive. However, the most effective method of reducing the surface area available for evaporation is the use of a high bund.

The CIA *Refrigerated Ammonia Storage Code* requires that for a refrigerated atmospheric ammonia storage tank in the UK means must be provided to contain the liquid safely in the event of failure of the main tank. The two methods which are acceptable are the use of a double integrity tank or the use of a concrete wall of approximately the same height as the tank wall. For the latter it is recommended that the width of the annulus is 1.5 m. The *Code* recognizes that in remote locations a low bund may sometimes be acceptable.

22.18.5 Ancillary facilities

Ancillary facilities for refrigerated ammonia tanks include refrigeration systems. Accounts are given by C.C. Hale (1980, 1984), C.C. Hale and Lichtenberg (1990) and Herbertsson (1992).

Refrigerated ammonia storage requires the provision of refrigeration facilities to liquefy vapour boil-off caused by heat inleak. Where the storage is part of an ammonia manufacturing plant, the main ammonia refrigeration facility may be used with just a backup set for storage, but generally the facility is a dedicated one. The principal elements are the refrigeration compressors and the ammonia condensers. There may also be a purge system to remove inerts from the ammonia condenser or receiver.

22.18.6 Instrumentation

A refrigerated ammonia storage tank should be provided with suitable measurements and alarms on the liquid level, pressure and temperature in the tank, and on boil-off gas flow.

Principal features of the instrumentation are the arrangements to prevent overpressure and overfilling. Pressure control is an integral part of the refrigeration system and there may also be a pressure control valve for emergency venting to flare.

In addition to the usual level instrumentation, use may be made of an interlock system to prevent overfilling by the operator.

In a double wall or double integrity tank system, instrumentation may be provided to detect any leak into the annular space between the two tanks.

22.18.7 Pressure relief

The tank also requires pressure relief and vent disposal arrangements. Accounts are given by C.C. Hale (1974, 1980), J.R. Thompson and Carnegie (1989) and C.C. Hale and Lichtenberg (1990).

Pressure relief is provided by a pressure relief valve. Most tanks also have vacuum relief. Pressure/vacuum valves are a common method of providing both forms of relief.

Venting to atmosphere has been common practice, provided that the location is suitable and the venting is done at a safe height, but the trend is away from such venting. In the normal operation of refrigerated ammonia storage, however, there is very little venting. Vapour is reliquefied by the refrigeration set and returned as liquid to the tank.

The main requirement for venting is in an emergency. In many systems flares are provided to handle emergency venting. The flares may be on the tank, or inside or outside the bund. Venting to the flare may be by a separate pressure control valve rather than the main pressure relieve valve. Complete combustion of the ammonia flared, and avoidance of odour, is assisted by the addition of fuel gas.

22.18.8 Inspection

The inspection of refrigerated ammonia storage tanks presents a number of problems and needs to be governed by a well thought out policy. Accounts are given by Truscott and Livingstone (1978), Shah (1982, 1987), P.P. Briggs, Richards and Fiesinger (1986), W.G. Jones *et al.* (1989), Conley, Angelson and Williams (1991) and Squire (1991). Inspection practice is one of the topics covered in the surveys by Hale.

One type of problem is the determination of an inspection interval. A difficulty here is that the opening up of the tank system is liable to introduce oxygen into it and may thus itself become a cause of deterioration. Another is that the outage period can be several months. A third difficulty concerns the degree of confidence which can be placed in the predictive techniques.

The problem may also come in the form of a need to decide whether to open up a tank on a particular occasion. An account of a review of a particular refrigerated ammonia storage tank, its features and its hazards, has been given by Squire (1991), who describes the reasoning behind a decision not to open up the tank for inspection.

There are also problems in the reliability of inspection techniques, as described below.

The stages of decommissioning a tank for inspection and recommissioning it after inspection have been described by Shah (1982) and P.P. Briggs, Richards and Fiesinger (1986). The latter give an account of the arrangements for continuity, emptying and purging, tank entry and cleaning, inspection and repair, and purging and refilling.

22.18.9 Rollover

There has been some concern that in refrigerated atmospheric storage tanks temperature stratification

might occur, leading to 'rollover', which is defined as 'a spontaneous and sudden migration of a substantial mass of liquid ammonia from the bottom of the tank to the surface". The effect of rollover is to release large quantities of vapour which could overpressure the tank.

Rollover has been the subject of an investigation by the Ammonia Storage Committee, as described by Ball (1968b). Calculations showed that only a very small temperature gradient is required to initiate natural circulation and prevent temperature stratification. The calculations have been confirmed experimentally. It has also been shown, however, that there is a possibility of stratification in ammonia containing over 5000 ppm of water.

An account of conditions which might lead to what he terms 'thermal overload' has been given by Squire (1991). They includes the introduction of contaminated or wrong material such as wet ammonia or even water; the introduction of warm ammonia; or a strong heat input such as might occur through loss of thermal insulation.

22.19 Ammonia Storage: Stress Corrosion Cracking

As already indicated, stress corrosion cracking (SCC) has been a widespread problem in ammonia pressure storage vessels. Accounts have been given by W.D. Clark and Cracknell (1977), Truscott and Livingstone (1978), Lemoine *et al.* (1986), Loginow (1986), Stephens and Vidalin (1988), Byrne, Moir and Williams (1989), Appl *et al.* (1990), Burke and Moore (1990), Selva and Heuser (1990) and Conley, Angelsen and Williams (1991).

Although ammonia has been used without apparent problems in the chemical and refrigeration industries for many decades, the use of liquid ammonia for agricultural purposes, which began after the Second World War, saw a number of cases of failure in the vicinity of welds on the pressure vessels used. A survey by T.J. Dawson (1956) found that about 3% of these pressure vessels failed within 3 years of entering service. In the chemical industry, concern intensified in the 1970s. A 1982 survey by the American Institute of Chemical Engineers (AIChE), described by Blanken (1982) and referred to by Burke and Moore (1990), reported inspection results for 72 pressure storage spheres in 37 of which SCC had been found.

Extensive investigation, and in particular the work of Lunde (Lunde, 1984; Lunde and Nyborg, 1987, 1989, 1990) in the Kjeller Ammonia Stress Corrosion Project (KASP) has given a clearer picture of the conditions under which SCC occurs. This work has shown that (1) uncontaminated ammonia does not cause cracking, (2) contamination with oxygen at a concentration as low as 1 ppm promotes cracking and (3) 0.2% w/w water inhibits cracking in oxygen-contaminated ammonia in the liquid phase.

It is also necessary to consider the vapour phase. Even where the liquid ammonia contains water, SCC can occur in the vapour phase, where due to the vapour–liquid equilibrium relations the concentration of oxygen is some 650 times higher than that in the liquid phase, whilst the concentration of water is some 500 times lower.

The metallurgy of the steel is also a factor. SCC occurs more readily where stress relief has not been carried out and in high yield strength steels. Measures to prevent SCC are therefore the use of stress relief by post-weld heat treatment and of low yield strength steels.

With respect to crack growth, it has been found that under conditions typical of those known to cause SCC (3 ppm oxygen, 500 ppm water), crack growth rates are similar to those which occur in service, of the order of 2–6 mm/year, depending on the stress intensity. Crack growth rates tend to be rapid initially, but to decrease markedly over time.

Whereas SCC has been widespread in ammonia pressure storage vessels, this has not been the case with refrigerated atmospheric ammonia storage tanks—as recently as 1987 it was largely discounted (Blanken, 1987). However, SCC has now been found in refrigerated ammonia storage tanks, as described below.

22.19.1 Inspection and repair

There are a number of accounts of the inspection of pressure vessels and of refrigerated tanks for ammonia storage in order to detect SCC. Inspections of pressure vessels have been described by R.S. Brown (1982) and by Guth and Clark (1985). They illustrate both the procedures for isolation, emptying, purging and entry, and bringing back on-stream such storages, and the procedures for inspection and repair.

Brown describes the inspection and repair in 1978 of two ammonia spheres installed in 1961 and 1962. Although the recommendation in 1962 to maintain the ammonia water content at 0.2% was followed, the spheres may have contained some ammonia which did not contain water. The inspection was performed using both magnetic particle and dye penetrant methods and significant cracks were found, which were diagnosed as being due to stress corrosion cracking. A maximum crack depth of 7.8 mm, or 25% of the shell weld cross-section, was found. Repairs were carried out in accordance with the ASME *Boiler and Pressure Vessel Code* and the Compressed Gas Association (CGA) *Guidelines for Inspection and Repair of Cargo Tanks*. Cracks were removed by mechanical grinding or arc gouging to sound metal. The area was then pre-heated and weld repaired. Further inspection and repair were conducted in 1980.

Another instance of cracking in two ammonia spheres in 1982 is described by Guth and Clark. Acoustic emission was used to detect the faults. In one sphere the repair method used was to grind down to the parent metal, repair the weld and hammer to relieve stresses. In the other sphere the crack was ground out and the welder then pre-heated the metal, repaired it, and peened it.

The discovery of SCC in a refrigerated ammonia storage tank has been described by Byrne, Moir and Williams (1989). The tank in question was a 12 000 te tank at Seal Sands, acquired by BASF from another company. The previous owners had relied on acoustic emission testing to extend the inspection interval for the tank and had detected no SCC. An inspection performed by the new owners using magnetic particle inspection discovered SCC. The SCC was found to occur mainly at the site of internal cleats and was attributed to defective welding procedures, the effect of which was aggravated by the use of high strength steel. A detailed account of

the treatment of defects in this tank has been given by Selva and Heuser (1990).

Appl *et al.* (1990) have given an account of the inspection of two further refrigerated ammonia storage tanks owned by BASF. They describe in detail the taking out of service, preparation, magnetic particle inspection, repair and bringing back into service.

Principal techniques for the detection of cracks are magnetic particle inspection, dye penetrant testing and acoustic emission testing. The use of dye penetrant testing is described by Brown, but not by the other authors mentioned.

As already indicated, there is a view that acoustic emission testing is not a reliable method. Vessels with SCC may not produce significant acoustic emission. Furthermore, Conley, Angelson and Williams (1991) describe a case where it was found that acoustic emission activity was greater in a vessel which had been repaired than in one with SCC which had not been repaired.

The inspection technique mainly quoted is magnetic particle inspection. However, the same authors state that even this does not necessarily reveal all the defects and that different operators tend to produce different results.

22.19.2 Fracture mechanics

Fracture mechanics, described in Chapter 12, has been applied to SCC both in ammonia pressure vessels and refrigerated ammonia storage tanks.

Accounts of the application of fracture mechanics to ammonia pressure vessels have been given by W.G. Jones *et al.* (1989) and Burke and Moore (1990).

Byrne, Moir and Williams (1989) describe the application of fracture mechanics to the Seal Sands refrigerated ammonia storage tank. The task of removing all the defects found was enormous. The interest lay, therefore, in reducing this activity to an acceptable level. In many cases it was possible to determine that the crack would exhibit leak-before-break behaviour. Those cracks for which this could not be demonstrated were removed. Further details of this fracture mechanics work are given by Selva and Heuser (1990).

The use of fracture mechanics to set the inspection interval for refrigerated ammonia storage tanks is described below.

22.19.3 Control policy

The maintenance of the integrity of ammonia storage requires a policy for the control of SCC. Accounts of such policies have been given by W.G. Jones *et al.* (1989), Appl *et al.* (1990), Squire (1991) and Conley, Angelson and Williams (1991).

W.G. Jones *et al.* (1989) describe the policy of ICI for the control of SCC in ammonia pressure vessels. As stated earlier, the overall ammonia storage policy is to move away from pressure storage spheres to smaller fully stress relieved pressure vessels and refrigerated storage tanks. They postulate two extreme scenarios for pressure spheres. An unpurged, unlagged sphere handling imported ammonia from a variety of sources at relatively high temperature and without vapour export may well experience a comparatively high level of SCC, whereas a purged, lagged sphere handling site-produced ammonia at a low temperature with continuous vapour offtake may experience little, if any. Operational measures to control SCC include purging to remove oxygen, maintenance of the water content, and cooling of the liquid.

An account of policy at Dupont for the control of SCC in ammonia pressure vessels has been given by Conley, Angelson and Williams (1991). The approach includes the use of fracture mechanics to predict the probability of failure and to determine inspection intervals.

Appl *et al.* (1990) of BASF rehearse some of the problems of controlling SCC in pressure storage vessels. There are difficulties in excluding oxygen and in keeping the oxygen content of the liquid ammonia below 1 ppm. There are some applications for which the ammonia is required to be dry and for which a requirement to maintain a water content of 0.2% w/w is highly undesirable. They state that stress relief by post-weld heat treatment appears to be the only reliable way to avoid SCC and that, whereas it has been necessary to scrap an older ammonia sphere due to SCC, a new stress relieved sphere inspected after 2 years of operation has shown no SCC.

22.20 Other Chemicals Storage

The storage of particular chemicals involves in some cases features which do not occur in the storage of the materials so far described. The general characteristics and handling of some of these chemicals are described in Chapter 11. The account given here seeks to highlight some features characteristic of the storage of individual chemicals; no attempt is made to give a comprehensive treatment of the storage of any given chemical, which is covered in the code cited.

Table 22.11 lists some topics on storage dealt with in codes and guidance for particular chemicals.

22.20.1 Acrylonitrile

Guidance on the storage of acrylonitrile (AN) is given in *Codes of Practice for Major Hazards: Acrylonitrile* by the CIA (1978 PA11) (the CIA *Acrylonitrile Code*).

AN has a boiling point of 77.3°C . It is typically stored in atmospheric fixed roof storage tanks. An AN storage tank should be provided with a suitable bund.

AN has a tendency to polymerize rapidly under certain conditions and in bulk storage it needs to be stabilized. The *Acrylonitrile Code* mentions three stabilizers. One is the methyl ether of hydroquinone (MEHQ), which is used when the AN contains dissolved oxygen. Another is ammonia, which combines with AN to form stabilizing compounds and thus in due course becomes depleted. The third stabilizer is water, which at a concentration of 0.2% w/w confers a degree of stabilization. Strong alkali or peroxides should be excluded.

Under certain conditions a flammable mixture can form in the vapour space of the tank. Precautions mentioned in the *Code* are the safe location of the vent, the installation of a flame arrester on the vent and the inerting of the vapour space.

22.20.2 Ethylene dichloride

Guidance on the storage of ethylene dichloride (EDC) is given in *Codes of Practice for Major Hazards: Ethylene Dichloride* by the CIA (1975 PA13) (the CIA *Ethylene Dichloride Code*).

Table 22.11 *Some topics on storage covered in certain codes of practice and guidance documents for particular chemicals*[a]

	Acrylonitrile	*Ammonia*	*Chlorine*	*Ethylene dichloride*	*Ethylene oxide*	*Hydrogen fluoride*	*Phosgene*	*Vinyl chloride*
Storage	7	3	10	4	26	4	8, 11	4, 6
Siting		6, 22						
Design conditions		7, 22	10				3, 12	
Filling ratio			11			18	31	App. IV
Foundations		10, 25						
Bunds	8	10, 25						
Insulation		13, 25						
Pressure relief	8		15					
Instrumentation	8						12, 15	
Ancillary equipment		10, 25						
Drums and cylinders	8, 10				27		29	
Stabilization	7							
Terminals	9		2, 20		19			15

[a] The entries give the page numbers. The documents referred to are as follows: acrylonitrile (CIA, 1978 PA11); ammonia (HSE, 1986 HS(G) 30); chlorine (HSE, 1986 HS(G) 28); ethylene dichloride (CIA, 1975 PA13); ethylene oxide (CIA, 1992 RC14); hydrogen fluoride (CIA, 1978 PA14); phosgene (CISHC, 1975/3); vinyl chloride (CIA, 1978 PA15). Aspects other than storage are considered separately in Chapter 11

EDC has a boiling point of 84.4°C. It is generally stored, dry or water saturated, in atmospheric storage vessels, which may contain several thousand tonnes. An EDC storage vessel should be provided with a suitable bund.

Under certain conditions a flammable mixture can form in the vapour space of the tank. The *Ethylene Dichloride Code* advises that consideration be given to protecting the vapour space from ignition and requires that means be provided for preventing over- and underpressure, including explosion relief.

Fire protection of larger EDC storage vessels tends to be by water spray systems, and that of small vessels is by fire insulation.

22.20.3 Ethylene oxide

Guidance on the storage of ethylene oxide (EO) is given in *Guidelines for Bulk Handling of Ethylene Oxide* by the CIA (1992 RC14) (the CIA *Ethylene Oxide Code*).

EO has a boiling point of −17.8°C. It is stored as a liquefied gas, mainly in pressure vessels, although refrigerated storage is an option. The separation distances appropriate for EO are of the same order as those quoted in codes for LPG, but should not be less than 15 m.

An EO storage vessel should be provided with a suitable bund. Since an EO spillage is commonly dealt with by dilution, the bund and drain arrangements should be able to handle water used for this purpose as well as the usual fire-fighting purposes of equipment cooling and fire control.

Many EO bulk storages are associated with plants which use a catalyst to polymerize the EO. Stringent precautions are necessary to ensure that the catalyst is excluded from the bulk storage. Three ways in which contamination may occur are (1) backflow from user plants, (2) introduction by a diluent gas pressurizing system, and (3) inadvertent contamination during supply offloading. Both design and operations measures are required to prevent contamination. The design measures are described in Chapter 11.

22.20.4 Hydrogen fluoride

Guidance on the storage of hydrogen fluoride (HF) is given in *Guide to Safe Practice in the Use and Handling of Hydrogen Fluoride* by the CIA (1978 PA14) (the CIA *Hydrogen Fluoride Code*).

HF has a boiling point of 19.5°C. Liquid HF is stored in pressure vessels of a few tonnes upwards.

The storage temperatures range from −5°C to 30°C, at which temperatures the vapour pressures of HF are 0.4 and 1.5 bara, respectively. Assistance is therefore required to effect transfer from storage, and this may be by the use of inert padding gas or, more commonly, by pumping.

The *Hydrogen Fluoride Code* lays particular emphasis on lines connected to the vessel below the liquid surface. Where these are unavoidable, it requires that there be a means of isolation integral to the vessel and independent of any external valve used for routine isolation and control, and that this external valve be capable of remote operation.

22.20.5 Oxygen

The storage of oxygen is the subject of two codes by the British Compressed Gases Association (BCGA) – *Bulk Liquid Oxygen at Production Plants* (BCGA, 1990 Code 20) and *Bulk Liquid Oxygen at Users' Premises* (BCGA, 1992 Code 19) – and of one by the National Fire Protection Association (NFPA) – NFPA 50:1990 *Bulk Oxygen Systems at Consumer Sites.*

The hazard posed by liquid oxygen is the reaction with combustible or flammable materials. The layout for the storage of liquid oxygen should include the use of non-combustible surfaces, the provision of separation distances between storages of liquid oxygen and flammable

liquids, and the prevention of contact between the two through flows of liquids, by ground contour or diversion.

22.20.6 Phosgene

Guidance on the storage of phosgene is given in *Codes of Practice for Major Hazards: Phosgene* by the CIA (CISHC, 1975/3) (the CIA *Phosgene Code*).

Phosgene has a boiling point of 8.2°C. It is stored as a liquid in pressure vessels.

The *Phosgene Code* advises that the storage temperature be kept below 8°C so as to reduce the load on the disposal system if the vessel has to be depressurized.

Particular emphasis is placed in the *Code* on the integrity of the pressure vessel, with requirements such as 100% radiography of butt welds and exclusion of installed lifting devices in the immediate vicinity of the vessel.

The *Code* requires that all branches in the top of the vessel be fitted with dip pipes which protrude at least to the maximum liquid level under normal operating conditions to ensure that the tank cannot be accidentally overfilled. There should be no lines connected to the vessel below the liquid surface, but if this is unavoidable they should be provided with a remotely operated isolation valve.

22.20.7 Monomers

An important class of liquid chemicals which require to be stored are monomers. Accounts of the storage of monomers is given by Shelley and Sills (1969) and Bond (1985 LPB 65).

A problem in the storage of monomers is polymerization. One hazardous consequence of such polymerization may be heat release, which causes both a rise in pressure and an acceleration in the reaction, resulting in the extreme case in the explosion of the tank. Another hazardous effect may be the blockage of vents and pressure relief devices.

It is common practice to dose monomers with additives. A discussion of their use has been given by Bond (1985 LPB 65). Types of additive include (1) inhibitors, (2) stabilizers, (3) anti-oxidants, (4) preservatives and (5) stenching agents. The function of inhibitors and stabilizers is to prevent polymerization, while anti-oxidants prevent decomposition, preservatives prevent bacterial or fungicidal attack and stenching agents impart an odour.

Typically, an inhibitor is effective only in the presence of oxygen. The use of nitrogen to blanket the liquid can reduce the oxygen content both in the liquid and in the vapour space and render the inhibitor ineffective in both phases. The liquid monomer may polymerize in a runaway reaction and the monomer vapour may polymerize and block vents.

A fuller account of the storage of monomers is given in the IChemE training package *Safer Use of Chemical Additives*, described in Chapter 27. This package includes a list of chemicals which are commonly dosed with an additive, and gives the purpose of the additive, an example of the additive used, the quantity added and an indication of requirement for dissolved oxygen.

The interactions between the various factors are illustrated by the account given by Shelley and Sills (1969) of options in the storage of styrene in the late 1960s. They describe the use of *p-t*-butyl catechol (TBC) as the inhibitor. The TBC also acts as an antioxidant but it is effective as an inhibitor only in the presence of oxygen. Storage under air suffices to maintain an adequate concentration of oxygen in the liquid phase. However, there remains the problem of polymerization in the vapour phase on the internal surfaces of the tank. This is liable to occur in older tanks with rusty surfaces, but is largely eliminated by coating the surface. One policy for older, uncoated tanks is the use of a nitrogen blanket, since in the absence of oxygen polymerization in the vapour phase is much reduced. Where such a nitrogen blanket is used, separate measures are taken to maintain the oxygen content of the liquid.

22.20.8 Vinyl chloride

Guidance on the storage of vinyl chloride is given in *Codes of Practice for Chemical with Major Hazards: Vinyl Chloride* by the CIA (1978 PA15) (the CIA *Vinyl Chloride Code*), and also in *Precautions against Fire and Explosion: Vinyl Chloride* also by the CIA (1978/12). An account is also given by Shelley and Sills (1969).

22.21 Bunds

An important form of secondary containment is a bund, or dike. Accounts of bunding are given in *The Design of Bunds* (Barnes, 1990 SRD R500) and *Bund Overtopping—The Consequences Following Catastrophic Failure of Large Volume Liquid Storage Vessels* (Wilkinson, 1991 SRD R530).

Barnes discusses: the bunding recommendations given in codes and standards; the philosphy of, and practice in, bunding; the design of bunds; the effectiveness and failure of bunds; and the use of high bunds and double integrity systems. He gives case histories of storage, and particularly bund, incidents and some statistics on storage failures. He draws particularly on the report *Liquefied Energy Gases Safety* (GAO, 1978) and on a study by Buckley and Weiner (1978).

Common practice is to provide a bund for refrigerated atmospheric storage of LPG and other LFGs and for ammonia, but not for pressure storage of LPG or ammonia.

For atmospheric storage tanks containing such hazardous chemicals as acids and alkalis it is again not usual to have a bund. If there is a danger of spillage onto roads, pathways or working areas, or of hazardous interaction between spillages of two liquids, separation by distance is appropriate.

22.21.1 Code requirements

Barnes reviews the requirements for bunding given in a large number of codes, including not only those for oil, LPG and LNG, but also for ammonia, chlorine and the various chemicals covered by the CIA codes. The overall picture is of considerable arbitrariness and some inconsistency.

Codes differ, for example, in their requirements for features such as capacity and permitted wall height. They even differ as to whether or not a bund is required at all. Liquid ammonia and liquid chlorine have similar adiabatic flash fractions, at 16% and 18.3%, respectively, but Barnes identifies one code for ammonia which recommends a high bund, and another for chlorine which

practically dismisses the use of a bund altogether. One code may set a maximum wall height to permit fire fighting in the bund, which would rule out the use of a high bund recommended in another code.

22.21.2 Philosophy of bunding

Barnes attempts, therefore, to develop a more coherent philosophy of bunding. He distinguishes between: liquids which are (1) flammable, (2) toxic, (3) corrosive and (4) reactive; liquids which are stored at a temperature (1) above the boiling point and (2) below it; and liquids which have (1) a high vaporization rate and (2) a low vaporization rate. Figure 22.20 shows his three decision trees for flammables, toxics and corrosives.

He takes a reactive material as being one which does not in its own right present a flammable, toxic or corrosive hazard, but which on contact with some other material, such as water or acidic or alkaline effluent, could produce a substance which does constitute a hazard. For this case he gives a simple two-branch tree, in which bunding is not required if the reactive material could not come into contact with another reactant but may be required if it could, depending on the assessed hazard.

22.21.3 Bund design

The elements of bund design which Barnes addresses are (1) bund capacity, (2) materials of construction, (3) wall design, (4) surface water drainage and (5) common bunding.

Codes differ in their recommendations on bund capacity which vary between 75% and 110% of the nominal capacity of the container protected. Barnes also quotes data from the General Accounting Office (GAO) report which illustrate the capacity allowed in practice. For the nine storages for which information is given, the capacities range from 50% to 139%.

In the selection of materials of construction, factors which have to be considered are the mechanical strength, the vaporization rate and, for low temperature liquids, the resistance to thermal shock. The materials used both for bunded areas and for bund walls are mainly earth and concrete. Use is also made of insulating concrete.

A low bund wall facilitates firefighting, and up to about 1980 many codes set a maximum height for the bund wall, often of the order of 2 m. This restriction is now less common, reflecting a trend towards high wall bunds. Codes may also set a minimum height for a bund wall, such as the 1.5 m height set in the NFPA codes.

Most codes do not give clear guidance on the arrangements for the drainage of surface water. A major problem here is that if the arrangement for the removal of rainwater is through a drain hole with a valve on it which should normally be kept closed, the valve is liable to be left open, thus allowing any liquid released into the bund to escape from it.

The use of common bunding is widespread, but it is not regarded as good practice to co-bund incompatible materials.

22.21.4 Bund sizing

Relations for bund sizing have been given by Barnes, and reformulated by Wilkinson. Following the latter, for a cylindrical tank in a circular shaped bund

$$\pi R^2(H-h) = \pi(R+L)^2 h - \pi R^2 h \qquad [22.21.1]$$

whence

$$h \geq R^2 H/(R+L)^2 \qquad [22.21.2]$$

where h is the height of the bund, H is the original height of the liquid, L the distance between the tank wall and the bund and R is the radius of the tank. For a rectangular bund

$$\pi R^2(H-h) = xyh - \pi R^2 h \qquad [22.21.3]$$

whence

$$h \geq \pi R^2 H/xy \qquad [22.21.4]$$

where x and y are the dimensions of the bund walls.

22.21.5 Vaporization from bunds

For many hazardous materials the magnitude of the consequences of a release depends largely on the rate of vaporization from the pool formed. In the main, this depends partly on the area of the bund and partly on the material of construction used.

A high bund gives a much smaller total area for vaporization. Another approach applicable with a low bund system is the use of a ditch within the bund, which for all but the largest releases, reduces the effective area for vaporization. There are a number of bund floor materials, such as insulating concrete, which give an appreciable reduction in the rate of vaporization. Another approach to the reduction of vaporization is to blanket the liquid surface, either with foam or with plastic spheres.

Vaporization from surfaces such as bund areas is discussed further in Chapter 15.

22.21.6 Spillage from bunds

With a low bund system in particular, if the release of liquid is sufficiently large it may flow as a wave which overtops the bund wall. Such overtopping has occurred in a number of cases. One of the most dramatic was at Qatar, where an LPG storage tank contained in a 50% capacity bund suffered a catastrophic failure. A 'tidal wave' of LPG overtopped the bund and caused massive destruction. Barnes quotes an estimate that, even if the capacity of the bund had been 100%, it would still have been overtopped by a wave some 5 m high.

Another major overtopping, from a bund that was 20% undersized, occurred at Moose Jaw, Saskatchewan, in 1980, following the catastrophic failure of an oil storage tank.

The GAO study gives results of modelling of bund overtopping by a tidal wave at a number of particular facilities. The six results for low bunds quoted by Barnes indicate overtopping in each case, with an average overspill of 58% of the tank contents.

Further work on overtopping of low bunds has been done by Greenspan and Young (1978), who derived an analytical model based on the shallow water equations, and by Greenspan and Johansson (1981), who performed model experiments. They correlated the fraction Q of the original liquid volume which spills over as function of the ratio h/H, where h is the height of the bund and H is the original height of the liquid in the tank, with the bund r radius and wall angle θ as parameters.

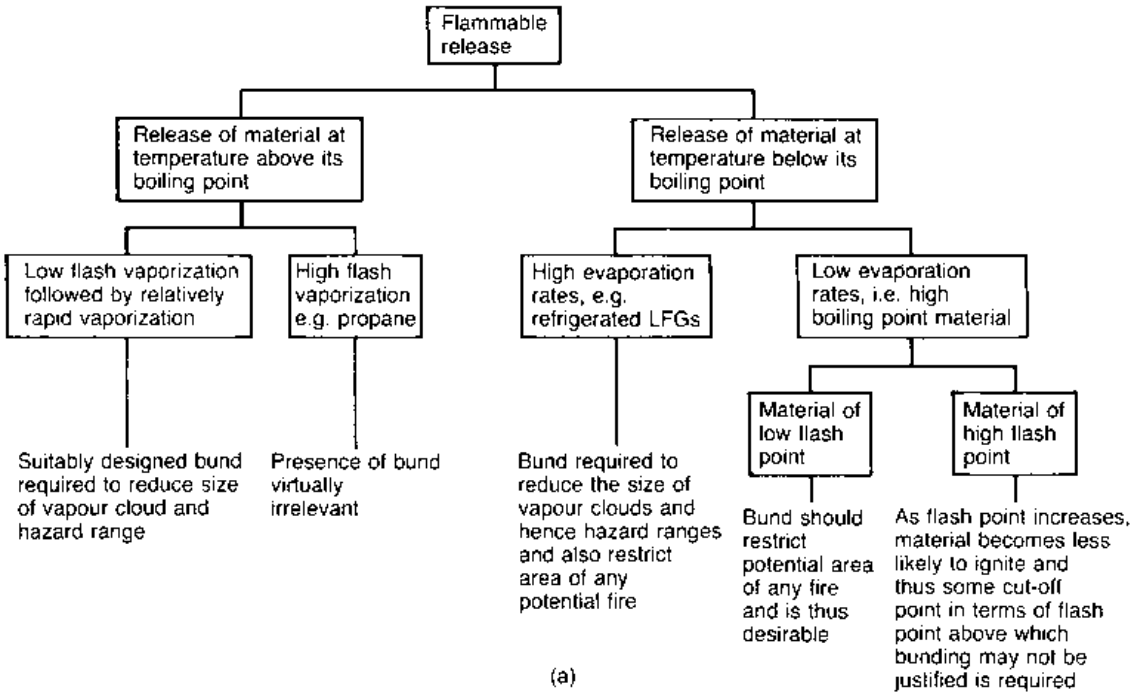
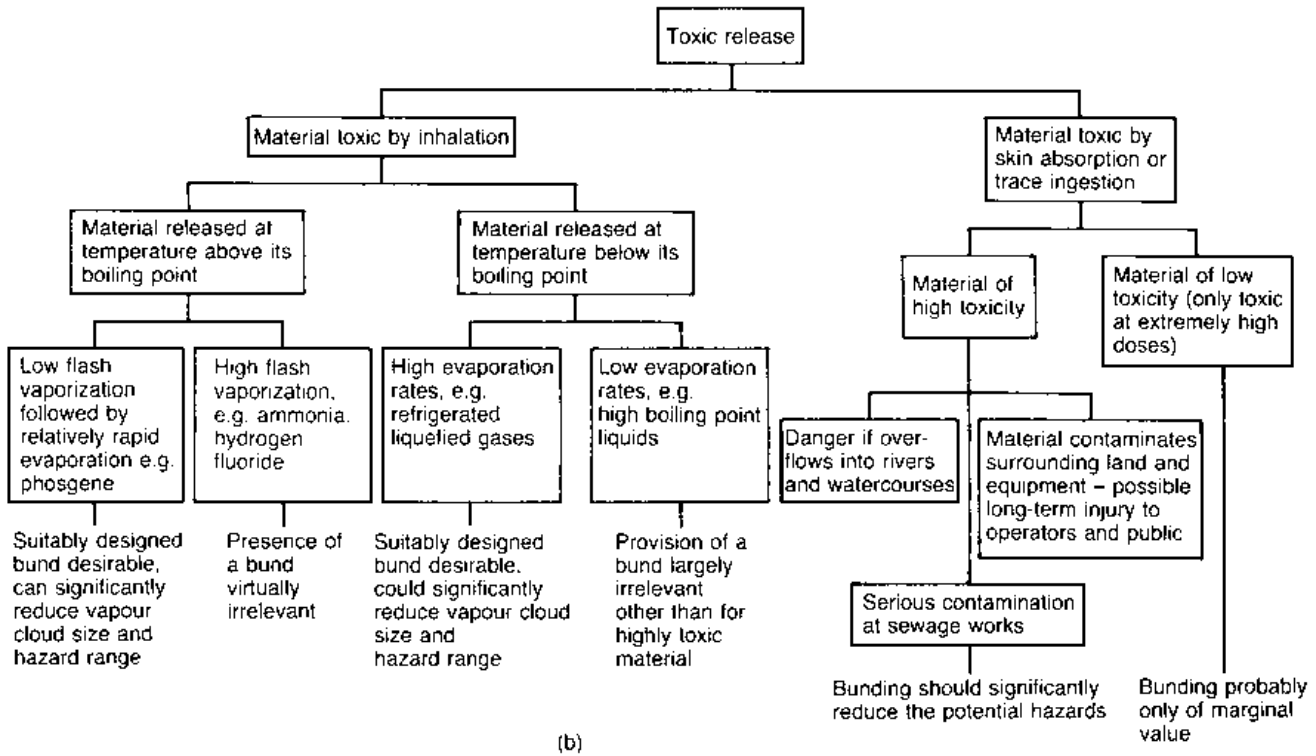


Figure 22.20 *Decision trees for the design of bunds (Barnes, 1990 SRD R500): (a) flammable material; (b) toxic material; and (c) corrosive material (Courtesy of the UKAEA Safety and Reliability Directorate)*



(b)

Figure 22.20 *continued*

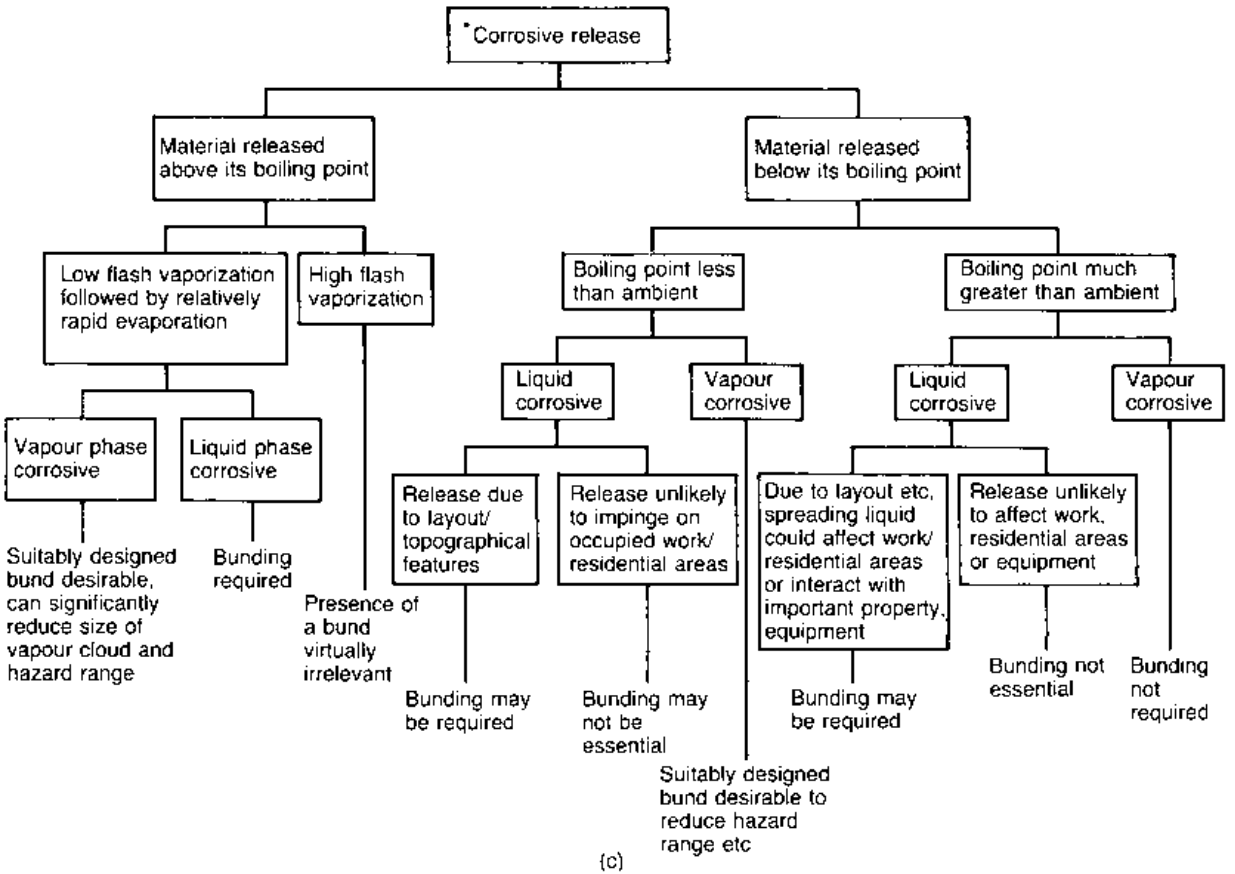


Figure 22.20 *continued*

Another form of escape from a bund is spigot flow in which the liquid issues from the containment as a jet which has a 'throw' sufficient to carry it over the bund wall. Spigot escapes also are dealt with in the GAO report.

22.21.7 High bunds

There is an increasing tendency to install high bunds, for which there are two main designs. In the first, the bund is some one-half to two-thirds the height of the tank wall and located about 7–8 m from it. In the second the bund is the full height of the tank and separated from it by a distance of 3 m or less. There may be a weathershield between the tank and the bund so that the existence of a separate bund is not obvious. In both designs the bund is structurally independent of the tank.

Storage systems with bunds are to be distinguished from double integrity tanks which have two walls, both capable of containing the liquid, and in which the outer wall is concrete.

22.21.8 Dynamic loading of bunds

If a sudden, catastrophic failure of the tank wall occurs, and a large release of liquid occurs, the bund is subject to a dynamic load. It has been common to design bunds for the hydrostatic load of the liquid in the tank, but not for this dynamic load. Attention was drawn to the problem by Cuperus (1979, 1980), and it has subsequently been the subject of a number of studies.

Most of the work has been done in respect of double integrity tank systems rather than bunds. For such a system Cuperus concluded on the basis of modelling work that the impact loading was highly asymmetric and that the pressure at the base of the outer wall could be six times the hydrostatic pressure of the stored liquid.

Adorjan, Crawford and Handman (1982) have modelled the behaviour of the release allowing for the resistance of the insulation between the two walls. This modelling has been extended by Vater (1985) using the basic relation

$$h\rho - \frac{\rho u^2}{2g} = (M_f + M_s)\frac{du}{dt} - R(x) \qquad [22.21.5]$$

where g is the acceleration due to gravity, h is the initial height of the liquid in the tank, M_f is the effective fluid mass, M_s is the effective mass of the tank shell, R is the resistance to flow, t is the time, x is the distance, u is the velocity and ρ is the density of the fluid. Solution of the equation requires the determination of the initial acceleration du/dt, for which the techniques of finite difference hydrodynamic analysis were used.

Finite difference studies on this problem have also been described by Trbojevic and co-workers (Trbojevic and Maini, 1985; Trbojevic and Gjerstad, 1989; Trbojevic and Slater, 1989). These authors have investigated both double integrity systems and bunds. Figures 22.21 and 22.22 show typical results for a high bund and a low bund, respectively.

Vater found that for the specific example which he considered the pressure at the base of the bund due to dynamic loading was some 2.65 times that due to hydrostatic load. The value obtained by Trbojevic and Gjerstad was 2.5. Higher load amplifications were found higher up the bund wall.

22.21.9 Consequences of spillage

A study of the consequences of spillage over a bund wall has been made by Wilkinson (1991 SRD R530). Predictions are given for the hazard ranges for various materials and scenarios using the GASP code for vaporization and the DENZ and CRUNCH codes for dense gas dispersion.

22.22 Underground Storage Tanks

Over the last 15 years there has come to prominence, particularly in the USA, the problem of leakage from underground storage tanks (USTs).

Underground storage tanks are treated in *Underground Storage Systems* (Schwendeman and Wilcox, 1987). Further accounts are given by Dwyer (1985), D.L. Russell and Hart (1987) and Semonelli (1990).

In the USA, the Resource Conservation and Recovery Act (RCRA) was amended in 1984 to extend the responsibilities of the Environmental Protection Agency (EPA) to underground storage tanks containing hazardous substances. Regulations on USTs came into force in 1988.

Various estimates have been given of the scale of the problem. The EPA has estimated that there are in the USA some 700 000 USTs of which about 25% are 'non-tight'. Evidence obtained by the EPA was to the effect that leaks came predominantly (84%) from loose tank fittings or faulty piping rather than from the tank itself.

The hazardous substances to which the controls apply are those given in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) list. A tank is defined as a UST if more than 10% of the volume of the tank and its pipework are below ground.

The regulations require that: new UST systems for hazardous substances have a secondary containment such as a double-walled tank, an external liner or other acceptable system; the piping have secondary containment such as double-walled piping or trench lining; and pressurized piping have an automatic leak detection system. The requirement for secondary containment of tank and pipework does not apply to new UST systems for petroleum. For these the requirements are for: periodic monitoring to detect leaks on the tank; periodic leak-tightness testing or monitoring on the piping; and, on pressurized piping, an automatic leak detection system. There are less stringent requirements for existing tanks.

Secondary containment systems are required to contain any leak until it is detected and removed, to prevent any release to the environment, and to be monitored at monthly intervals. Where external liners are used, they should be such that they surround the tank completely and prevent lateral as well as vertical migration of a leak; can contain the whole contents of the tank; and prevent interference of rain or groundwater with the ability to contain and detect a leak.

Design of UST systems and methods of leak monitoring are discussed by D.L. Russell and Hart (1987). The designs include: a reinforced concrete tank with an external liner; a fibreglass tank with an external liner; and a regular horizontal tank placed in a reinforced concrete secondary containment.

The authors discuss the methods available for leak detection. Volumetric leak detection techniques rely on

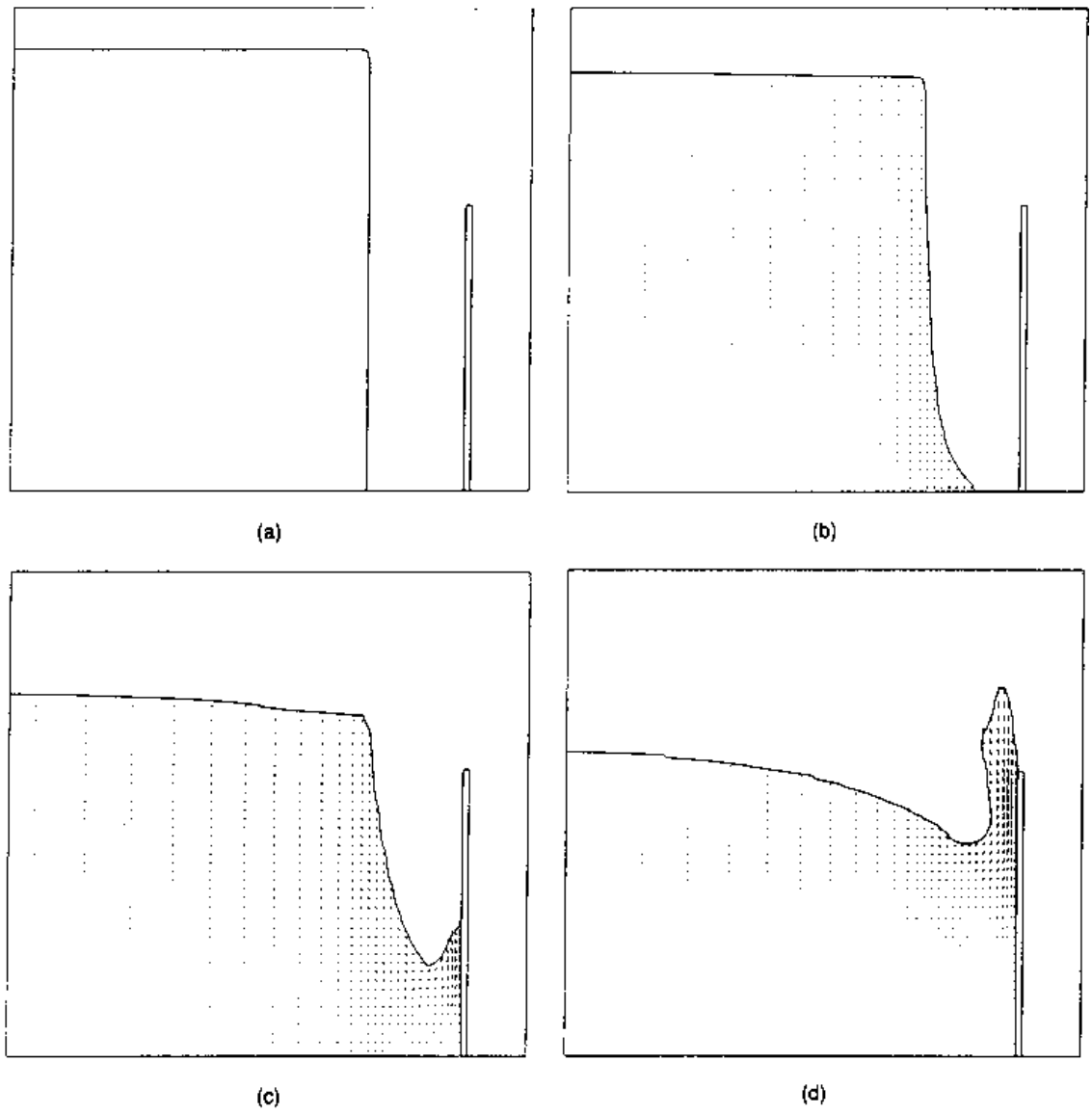


Figure 22.21 *Simulation of liquid behaviour following the failure of a single wall storage tank inside a high bund (Trbojevic and Slater, 1989): (a) time t = 0 s; (b) t = 0.6 s; (c) t = 1.2 s; (d) t = 1.8 s (Courtesy of the American Institute of Chemical Engineers)*

the change in level in the tank. Other techniques are based on detection of the leak itself. A further account of leak detection is given by Higgins and Byers (1989).

Methods used for decontamination of land where a UST has leaked are described by E. Johnson (1989a).

HSE guidance on underground storage tanks is given in HS(G) 52.

The environmental aspects of underground storage tanks are considered further in Appendix 11.

22.23 Glass Reinforced Plastic Storage

Most storage is constructed in steel but widespread use is also made of glass reinforced plastic (GRP), or fibre reinforced plastic (FRP), containments.

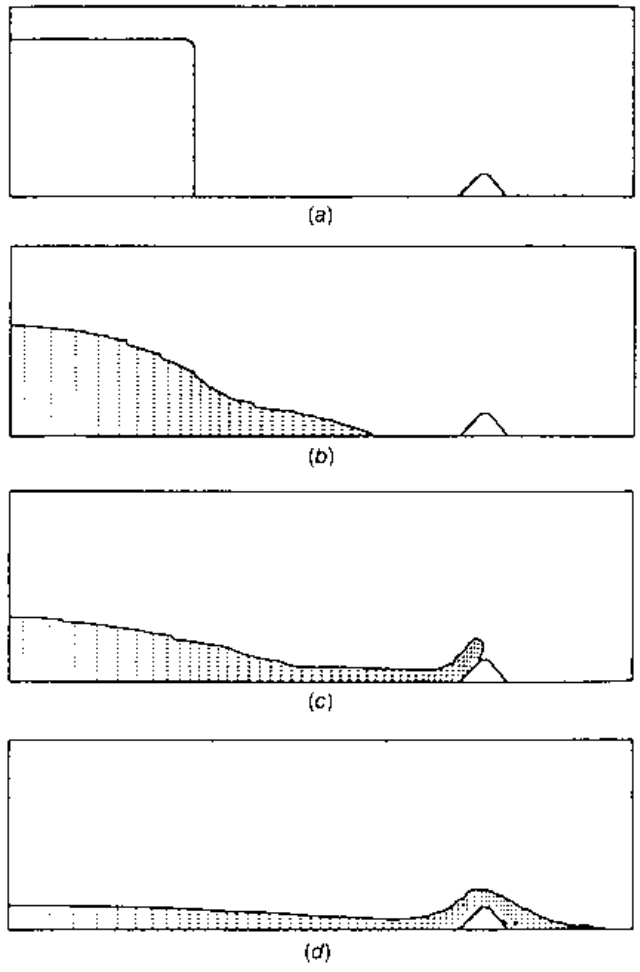


Figure 22.22 *Simulation of liquid behaviour following the failure of a single wall storage tank inside a low bund (Trbojevic and Slater, 1989): (a) time t = 0 s; (b) t = 1.5 s; (c) t = 2.5 s; and (d) t = 4.0 s (Courtesy of the American Institute of Chemical Engineers)*

An account of the use of GRP containers in the process industries is given in *Composite Materials Handbook* (Schwartz, 1991). HSE guidance on GRP containments is given in PM 75 *Glass Reinforced Plastic Vessels and Tanks: Advice to Users* (1991).

The design of GRP containment is governed by BS 4994: 1987 *Specification for Design and Construction of Vessels and Tanks in Reinforced Plastics.*

GRP tanks and vessels are widely used to store corrosive materials. In addition to good corrosion resistance, they have the further advantage that they are readily fabricated into complex shapes. GRP does not suffer from external corrosion and it can have a suitable self-colouring. These factors minimize the maintenance costs of GRP storage.

However, GRP tanks are not without their hazards. In a small but significant number of instances tanks have failed. Some of these have been outright, or catastrophic, failures which have released the entire contents. The resultant tidal wave of liquid is capable of demolishing a bund wall, or, if the tank is indoors, a building wall.

GRP is subject to creep under sustained load, it is susceptible to chemical attack and some types may fail at temperatures below 100°C.

Typically, a GRP tank failure is due to environmental stress cracking in which the tank is subjected to

excessive stress and crack propagation occurs, at first slowly and then with increasing rapidity. Prior to failure the tank often exhibits leaking or 'weeping'.

Resin rich layers are used to protect the glass reinforcement. Matrix cracking can expose the glass fibres to chemical attack.

Another cause of failure is excessive temperature. There have been cases where a GRP tank containing water has failed at 70°C.

As a material of construction GRP has a number of features which distinguish it from steel. One is that it is anisotropic and thus has different strengths in different directions. The degree of difference depends on the fabrication, but it can be significant. Compared with steel, GRP is softer, it can only withstand much lower temperatures and it has a lower impact resistance but a coefficient of expansion three times higher.

Different GRP formulations are required for the containment of different chemicals. With an incorrect material deterioration can be caused by even small traces (ppm level) of impurity. This has obvious implications for the change of use of tanks and for the use of second-hand tanks.

GRP tanks are often provided with liners.

PM 75 describes the salient features of safety in the use of GRP storage, covering design, fabrication, installation and operation.

Design and fabrication should be to BS 4994: 1987, which grades GRP containments into three categories, Categories I–III. The strictest requirements are those for Category I, the application of which is governed by factors which include size, operating conditions and hazards.

Important features of the design are the use of the correct material and the limitation of the liquid temperature. PM 75 advises that the operating temperature should not exceed the design limits and should be no higher than 110°C.

The purchaser of a GRP tank should supply the manufacturer with a full specification of the tank duty. PM 75 reproduces from BS 4994 an appendix giving the suggested information.

Design and installation should ensure that the tank is not overstressed by providing good support for both the tank itself and the attached pipework. Care should be taken to avoid damaging the tank during erection.

In service the tank should be subject to periodic inspection. Inspection techniques used include: ultrasonics to assess wall thickness, etc.; acoustic emission monitoring to detect defects; spark testing of welds and liner adhesion; and surface hardness testing and strain measurement.

22.24 Filling Ratio

The maximum permissible working capacity of a storage vessel, or permissible fill, is generally expressed either in terms of the filling ratio or of the maximum permissible volume. Other measures used are the filling density and the filling volume.

Filling ratios for transport of liquefied gases by road in the UK are given in BS 5355: 1976 *Specification for Filling Ratios and Developed Pressures of Liquefiable and Permanent Gases*. This standard gives formulae for the determination of the filling ratio, guidance on reference temperature for the UK and on maximum shade temperatures in other countries, and values of the filling ratio for the UK. It is considered further in Chapter 23.

The formula used to calculate the filling ratio is generally of the form

$$\eta = \frac{\rho_p}{\rho_w}(1 - \phi) \qquad [22.24.1]$$

where η is the filling ratio, ρ_p is the density of the liquid at the reference temperature, ρ_w is the density of water at 15°C and ϕ is the fractional free space. The formula may also include a term for the confidence limits on the density of the liquid. The reference temperature is the maximum temperature which the product should reach in service.

For the UK, BS 5355: 1976 gives for low pressure liquefiable gases in vessels of volume greater than 5 m^3 a reference temperature of 38°C. The corresponding shade temperature is given as $\leq$35°C.

Filling ratios for LFG storage vessels are given in the ICI *LFG Code*. The *Code* takes for LFG a free space of 3% and a reference temperature of 38°C for vessels over 5 m^3. This yields the following filling ratios:

Propane	0.46
Propylene	0.475
n-Butane	0.54
Vinyl chloride	0.85

A formula for the maximum filling capacity of LPG storage vessels is given by the LPGA (1991 COP 1). This is

$$U_{max} = 0.97 \frac{g_i}{g_t} V \qquad [22.24.2]$$

where g_i is the specific gravity of the liquid at the reference temperature, g_t is the specific gravity of the liquid at its lowest likely temperature at filling, U_{max} is the maximum permissible volume and V is the internal volume of the vessel. The lowest likely temperature at filling is usually taken as 5°C.

It should be noted that whereas in Equation 22.24.1 the denominator is the density of water at 15°C, in Equation 22.24.2 it is the density, or rather specific gravity, of the liquid in question at the filling temperature.

Guidance on filling density is given for LPG in NFPA 59 and for LNG in NFPA 59A. Guidance on the filling ratio for chlorine is given in the CIA *Chlorine Code*.

22.25 Loading and Unloading Facilities

Closely associated with bulk liquid storage are the arrangements for the loading and unloading of road tankers and rail tank cars. An appreciable proportion of accidents occur in the unloading and loading facilities.

Guidance on loading and unloading facilities is given for petroleum products in NFPA 30, the IP *Refining Safety Code* and HS(G) 50 and HS(G) 52; for LPG it is given in NFPA 58 and 59, the LPGA *LPG Storage Code*, the IP *LPG Storage Code* and HS(G) 34; and for toxic materials in general in the CCPS *HTHM Storage Guidelines*, for ammonia in HS(G) 30 and for chlorine in HS(G) 28. Hazardous area classification is covered in the IP *Area Classification Code*. Further guidance is given

by the Oil Industry Association (OIA, Pub. 711) and in the ICI *LFG Code*.

The account given here is concerned with the loading and unloading facilities associated with bulk storage in the main process industries, essentially at sites where the facilities and systems of work are those that are normal in these industries. It does not deal with facilities at small sites such as petrol filling stations.

It is convenient to consider first facilities in general terms, but with reference essentially to road tanker facilities for petroleum products, and then to deal with aspects specific to rail tankers and to particular chemicals.

22.25.1 Hazards

Before considering the facilities as such, it is worth reviewing some of the hazards which are characteristic of unloading and loading facilities. There are four broad categories of hazard at a tanker terminal. These are fire/explosion from leaks and spillages, fire/explosion of product in the tanker, toxic release and accidents arising from the transfer of the wrong products.

These hazards arise from: (1) overfilling of the container; (2) failure of the connection; (3) damage caused by movement of the vehicle itself; (4) vehicle movement whilst connected; (5) damage caused by impact by other vehicles; (6) ignition by static electricity; (7) equipment failures; (8) misidentification; and (9) maloperation.

Overfilling of the tank during loading of the storage vessel is one of the most common accidents at such facilities, as witnessed by the extent of the measures taken to counter it. The temporary connections between the tank and the storage are a weak link, and again attract much effort to maintain their integrity. A particular cause of failure with some connections is a lack of flexibility to accommodate the normal movement of the tank on its suspension during the transfer operation.

Damage may be done to the fixed plant or to the vehicle itself as it moves to and from the loading bay. Releases also occur due to the movement of the vehicle whilst still connected to fixed system. This occurs most commonly when the vehicle is driven off, but other causes can be an unsecured vehicle on unlevel ground or impact by another vehicle. Impact by another vehicle may also lead to a release due to the rupture of the connections.

Any of the releases described may result in a fire, or occasionally an explosion. Another cause of fire/explosion is ignition of a flammable mixture in the tank of the vehicle.

22.25.2 Fire and explosion

A fire/explosion of the product during top loading constitutes a serious problem. The type of product which is the most hazardous is one which gives a flammable mixture in the vapour space. Liquids which give a lean mixture below the lower limit or a rich mixture above the upper limit of flammability are less troublesome.

Ignition of the product is usually due to static electricity. This may be generated if the liquid is allowed to fall free and splash from the filling pipe into the tank, so it is normal practice to position the tip of the filling pipe near the bottom of the tank. But charge may be generated at the start of the filling before the pipe is fully submerged. It is also possible for the liquid to acquire a charge before it reaches the tank. Build-up of charge due to flow in the pipe itself is usually not critical, but product filters with cotton, paper or felt elements are prolific generators of static electricity. It has usually been considered that a relaxation time of 30 s between the filter and the outlet of the filling pipe is necessary to dissipate this charge. Moreover, there has been a trend to purer, drier products for which the relaxation time tends to be in the range 100–500 s. A fuller account of the hazard of ignition by static electricity, including the specific case of tanker loading, is given in Chapter 16.

Fire/explosion also occurs due to spillage. Hose spillages are particularly frequent. Often they occur because a tanker is driven away from the gantry with the hose still connected. Also, hoses may burst because they are not strong enough.

22.25.3 Switch loading

A particularly hazardous situation occurs when a less volatile product is put in a tank which previously contained a more volatile one. This hazard is described by the OIA. There is often a tendency for the residue of the latter to form a flammable mixture, while the former does not readily dissipate static charge. According to the OIA, such 'switch loading' has accounted for some 70–80% of severe losses at loading bays. These appear to occur most often when compartments are one-quarter to one-third full and when temperatures are close to 30°F (−1°C).

The IP *Refining Safety Code* states that, wherever possible, switch loading should be avoided.

22.25.4 Siting

Since loading and unloading facilities are areas of relatively high risk, their siting is important. A suitable approach is to locate the facility on the far side of the storage from the process, where this is practical. The location should also be chosen to allow good access for the vehicles to be loaded or unloaded, but to be as free as possible from any form of interference, particularly from other vehicles. Siting is considered in more detail in Chapter 10.

22.25.5 Layout

The layout of the loading and unloading facilities can make a major contribution to the elimination and minimization of incidents. Some aims of layout are to avoid releases, to minimize the size of any release, to prevent the ignition of a release, and to control any fire from an ignited release.

Some features of layout which contribute to these aims include: (1) minimum separation distances, (2) the general form of the loading/unloading bay, (3) ground slope and drainage, (4) ventilation, (5) access and escape, (6) lighting, (7) routing of pipelines, (8) protection against vehicle impact, (9) control of movements of vehicles, (10) control of the movement of personnel, (11) vessel, connection and equipment identification, (12) direct lines of sight, (13) control of ignition sources, including hazardous area classification, (14) fire protection and (15) emergency equipment.

Minimum separation distances for the loading and unloading facilities for particular materials are given in the codes for those materials, as described in Section 22.26.

There should be sufficient space so that congestion is avoided. It is desirable that vehicles are able to drive in and out without reversing. The ground at a loading/unloading bay should be firm and impervious. At the filling point it should slope away so that spillage does not collect under the tanker and there should be suitable drainage. Where top loading is practised, there should be a platform with good access, including access to the top of the tanker, and a means of escape. The facility should be well ventilated and well lit.

The layout should assure protection both of the fixed equipment and of the tanker from impact by another vehicle. Attention should be paid to the routing of pipelines connected to the facility. Damage from vehicles can largely be avoided by the provision of high kerbs around the loading island and also of barriers to protect equipment and by controlling the movement of vehicles. It may also be necessary, particularly where other persons may be passing, to provide barriers or other means to control vehicle movements.

Storage vessels, filling connections and other equipment such as pumps should be provided with a means of identification. The layout should provide direct lines of sight so that personnel conducting transfer operations can observe the effects of their actions.

Where a fire hazard exists, the control of ignition sources should be exercised through hazardous area classification and fire protection facilities should be provided. The hazardous area classification of loading and unloading facilities is considered in Section 22.25.6 and fire protection is discussed in Section 22.25.11.

Emergency equipment appropriate to the material handled should be available at the facility.

There should be arrangements at a filling point to run part or all of tanker's contents back to the storage vessel if necessary.

22.25.6 Hazardous area classification

Loading and unloading facilities are among the cases dealt with by the method of direct example in the IP *Area Classification Code*, which covers petroleum products. The code gives detailed recommendations for the hazardous area classification (HAC) of road and rail transportation, dealing separately with loading and unloading, including the unloading of road tankers at petrol filling stations. The *Code* gives some ten figures showing the HAC zoning in plan and elevation for different facilities and situations.

Further guidance on the HAC for petroleum products is given in NFPA 30 and guidance on the HAC for LPG is given in HS(G) 34 and NFPA 58 and 59.

22.25.7 Filling arrangements and connections

There are three main types of connection used for the transfer of liquids between the fixed facility and the tank of the vehicle. These are (1) flexible hoses, (2) articulated arms, and (3) flexible couplings. A description of the three types of system as used for chlorine is given in HS(G) 28.

Connection is frequently be means of a hose. Articulated arms with swivelled joints are used on installations with a high throughput. Flexible couplings are used for certain products such as chlorine.

Good practice in respect of hoses is illustrated by the guidance given in HS(G) 34 on flexible hoses for LPG. A hose should be designed and made to an appropriate standard such as BS 4089; it should be suitable for the product to be handled; it should be provided with means of identification; it should be protected both in respect of its end fittings against damage and ingress of foreign matter and, where necessary, in respect of external damage, using a procoil or similar device; it should be subject to a full system of maintenance and test, including inspection records, annual hydraulic testing, periodic examination for kinks, weakness and end fitting deterioration and electrical discontinuity; and it should be kept in a safe place when not in use and replaced or repaired when worn or damaged.

The filling of tankers is carried out through a pipe in the top or in the bottom of the tank, i.e. by top or bottom loading. Top loading is often done by a rigid arm system and bottom loading by a hose. Pipes should be arranged so that the line between the tanker and the plant can be emptied before the tanker is uncoupled. Incidents sometimes occur due to a failure of the hydraulic system on a filling arm which causes it to drop and foul a tanker, and a locking device should be provided to prevent this.

Vapour recovery systems are becoming more widely used, mainly to meet pollution requirements. These systems have a filling arm which makes a gas-tight fit over the tank hatch, a short pipe which gives splash filling and a float switch which cuts off the flow when the tank is full. There is a separate vapour line which goes to a compressor and gasholder. Loss experience with these devices is good.

22.25.8 Shut-off arrangements

There are measures which can be taken to avoid overfilling and a number of devices which can be used to effect rapid shut-off if a leak occurs due to overfilling, failure of a filling connection or otherwise.

These include (1) vessel identification, (2) vessel sizing, (3) ullage control, (4) pre-set filling meters, (5) pump trips, (6) high level alarms, (7) dead man's handle arrangements, (8) non-return valves, (9) excess flow valves, (10) remotely operated isolation valves, (11) remote control of pumps and (12) self-sealing couplings.

The marking of vessels to ensure correct identification is one elementary measure to prevent releases. The use of a storage vessel with a capacity at least that of the largest tanker from which transfer may be attempted is another: this is particularly important for chlorine facilities. Attention to the ullage in the container to which transfer is to be made is a third.

A pre-set filling meter may be used to ensure that the quantity transferred does not exceed the capacity of the container. The filling pump may be provided with a trip to stop the pump and preferably close a shut-off valve when the pre-set quantity has been delivered. There may also be a manual control for the pump and the shut-off valve at the loading point. On storage a high level alarm may be provided to warn if overfilling is occurring.

An arrangement which guards against an operator starting the filling and then having his attention diverted elsewhere is the use of a spring-loaded self-closing filling

valve which remains open only as long as the operator's hand is on it, i.e. a dead man's handle valve.

Means are available for cutting off flow from a damaged or disconnected connection, e.g. non-return valves, excess flow valves and remotely operated isolation valves.

Whatever the other arrangements, means should be provided for stopping all pumps immediately if an incident occurs. This should be a manual control in an attended terminal and an automatic one in an unattended one.

As described below, another means of shutting off a leak, applicable to the case where the vehicle moves away whilst still connected, is the use of a self-sealing coupling.

22.25.9 Vehicle control

Likewise, there are a number of methods which can be used to prevent a vehicle from moving away whilst it is still connected to the fixed plant by a filling connection, and thus causing a release. These mostly involve some form of interlock. There are also devices to shut off flow.

The measures used differ somewhat between road and rail, and those described here are those applicable to road tankers. The ground at the filling point should be level and chocks should be used to hold the tanker in position.

Movement of the vehicle may be prevented by the use of an interlock system. One method is the use of an interlocked barrier. Another is an arrangement which locks the vehicle's braking system when the delivery hose is taken from its stowage position and releases the system only when the hose is restowed. A third is a brake flap arrangement which must be moved aside to gain access to the filling branch, the action of which actuates the vehicle's braking system.

Flow may be cut off if the tanker moves by use of a self-sealing breakaway coupling. Other emergency shut-off devices have already been described.

22.25.10 Static electricity control

There are various precautions which may be taken against the hazard of ignition of product by static electricity. An account of these measures is given by the OIA. Two measures which it considers very desirable, although they are not generally adopted, are the complete elimination of switch loading and the use of inerting of the tank during filling. The latter tends to be rather expensive and time-consuming.

Measures which are normally taken are earthing and bonding to dissipate static charges on the metal containment. The filling pipe, the product line and the gantry should be electrically continuous and earthed. The electrical resistance of the gantry should not exceed $10^4\ \Omega$ and should be checked periodically.

Bonding involves connecting the product line to the tank. This prevents static discharge between the filling pipe and the tank. It is usually done using a wire with alligator clips. It is considered adequate if the electrical resistance of the bond does not exceed $10^6\ \Omega$. The bond should be inspected and its electrical resistance checked periodically. The bond should be such as to avoid damage if the vehicle is driven off before the bond is disconnected. Devices which drop down from the gantry to touch the tank are not considered effective for bonding.

As mentioned in Chapter 16, however, it may be desirable to aim for lower electrical resistances than those just quoted in order to ensure that the latter are reliably achieved. The bonding should be attached before the filling pipe is inserted into the tank and it should remain in place until the operation is completed.

However, earthing and bonding do not immediately dissipate the charge on the surface of a non-conducting liquid in the tank. A relaxation time should be allowed after filling has been completed and before the filling pipe is withdrawn, to permit static charge on the liquid surface to dissipate to the pipe or tank shell. The minimum time is 1 minute, but longer periods are advisable with some products, as indicated above.

Where switch loading is practised, there are various additional precautions which may be taken. These include the use of inerting, low filling rates, special filling tips and static neutralizing devices, and longer relaxation times. The initial filling rate should be 3 ft/s maximum, rising to 15 ft/s when the filling pipe outlet is fully submerged. Special filling pipe regulator tips are available to give this initial flow limitation. Static neutralizers may be installed in the product line. Longer relaxation times may be allowed before withdrawing the filling pipe.

Bottom loading does not eliminate the static electricity hazard, particularly in switch loading, and still requires earthing.

With vapour recovery systems, splash filling would theoretically appear to increase the hazard on switch loading. The OIA therefore recommends against their use in switch loading situations.

22.25.11 Fire protection

A loading/unloading facility should be provided with appropriate fire protection. The arrangements depend on the particular installation and especially on the product transferred, the amount of material and the number of tankers handled, the location of the terminal, and the potential for damage and business interruption.

Fixed water sprays may be provided to cool tankers at filling points. The failure of tankers in a fire can be relatively rapid. The OIA makes recommendations for fixed sprays of water, foam or dry chemicals for terminals for flammable liquids. It is particularly concerned with automatic systems for unattended terminals. It suggests that fixed sprays should be located both in the roof and along the loading island so that extinguishing media can be directed under tankers. For fixed water sprays a rate of application of 0.25 USgal/ft^2 min over the whole loading area is recommended.

The ICI *LFG Code* recommends fixed water sprays for terminals handling more than one tanker simultaneously or more than four tankers per day. The rate of application of water should be 0.2 UKgal/ft^2 min of tank surface. In multi-bay installations there should be arrangements to control the sprays selectively. Automatic operation is not essential, as it is assumed that the terminal is manned during transfer operations.

The *Code* also states that if fixed water sprays are not provided there should be fire hydrants capable of the same rate of application of water, but that if fixed sprays are installed the hydrant capacity can be reduced by 50%.

For LFG fires the method of extinction is to cut off the supply of fuel. Water from spray nozzles may be used to cool tankers and equipment, particularly to prevent direct flame impingement, to bend flames away from equipment and to cool the flames themselves. But putting water directly on an LFG spillage has the effect of increasing the evaporation rate and this generally makes the fire worse. In addition, it is undesirable to extinguish an LFG fire with water because of the danger of a subsequent explosion. Water should not be used, therefore, on LFG fires, except for very small spillages. Foam may be used to limit the evaporation rate, but it will not normally extinguish a fire and, as just stated, it is not desirable that it should.

Portable fire extinguishers and sand should be provided for dealing with small spillages or vehicle fires.

Drains should be provided which will handle flammable liquids and fire water, along the lines previously described.

Electrical cabling should be routed outside the high risk areas of the terminal or should be protected so that emergency services are maintained and any subsequent interruption minimized.

It is desirable that the tanker at a terminal have some degree of fire resistance. There are large aluminium tankers which may fail within only 1 minute when exposed to intense ground fires and these represent a serious hazard.

The OIA draws attention to the increase in the number of unattended or 'keystop' terminals for flammable liquids. In such terminals there are problems of damage to loading equipment, of a lack of supervision of loading practices and of the absence of personnel to control fires.

22.25.12 Rail facilities

Most of the features of loading and unloading facilities for road apply also to rail, but there are some which are characteristic of the latter.

Rail tracks should be laid straight and level, though a small gradient can be tolerated. HS(G) 52 gives a limit of 1 in 400. The track and line-side equipment should be maintained to the appropriate British Rail standard.

There should be arrangements for the control of locomotives whilst filling is in progress.

There should be earthing and bonding to dissipate the static charges. Rails should be bonded together and to the product lines. A separate bond to the tank is necessary only if the earthing between the tank and the rails via the wheels is inadequate.

Stray currents constitute an additional hazard. These may arise from electrified main line tracks, rail circuit signal systems or cathodic protection systems. If the siding is part of an electrified system, it should be electrically isolated from the rest of the system and bonded to the site main earth. Precautions which may be necessary against stray currents are insulating inserts in the rails where they enter and leave the loading siding and an insulating flange between the product line and the filling pipe together with a flexible bond between the rail tank and the filling pipe.

22.25.13 Operation

As with other aspects of process installations, the safety of loading and unloading facilities depends as much on operation as on design.

A significant issue is the manning of the facility, which tends to vary and which has more than one aspect. One is control of the transfer. In some cases transfer is conducted by plant personnel and in others by the driver of the tanker. Another aspect is the back-up available if something goes wrong, such as the outbreak of a fire or a toxic release sufficient to overcome the person effecting the transfer.

Safe systems of work should be provided and enforced which cover all aspects of the operation, from the identification of materials, vessels, connections and equipment, through the transfer operations themselves, to the emergency procedures.

There should be a good standard of housekeeping at the facility.

During filling all ignition sources should be excluded from the area of the filling point, including road or rail traffic. The engines of road tankers should be turned off.

22.26 Loading and Unloading Facilities: Particular Chemicals

22.26.1 Petroleum products

As stated above, guidance on the loading and unloading facilities for petroleum products is given in NFPA 30, the IP *Refining Safety Code* and HS(G) 50 and HS(G) 52, and also by the OIA.

The account already given has been based largely on facilities for petroleum products and these may therefore be treated briefly. Features specific to such products given in the guidance just mentioned include: minimum separation distances; hazardous area classification; top and bottom filling arrangements; spillage disposal arrangements; and fire protection.

22.26.2 LPG

For the loading and unloading facilities for LPG, guidance is given NFPA 58 and 59, the LPGA *LPG Storage Code*, the IP *LPG Storage Code* and HS(G) 34, and also in the ICI *LFG Code*.

For LPG the requirements for minimum separation distances are different. Particular importance attaches to the arrangements for the control of ignition sources, including: the control of static electricity; hazardous area classification; and fire protection. The discussion of fire protection in Section 22.25 covers LPG facilities.

22.26.3 High toxic hazard materials

Guidance on the loading and unloading facilities for high toxic hazard materials (HTHMs) is given in the CCPS *HTHM Storage Guidelines*. In essence, the *Guidelines* cover ground similar to that just considered, both in respect of the hazards and the measures taken to control them, at least as regards loss of containment, though the hazard from the flammability of the material may not apply. It is worth emphasizing, however, that the points which do apply do so with particular force to HTHMs and that for such materials the standards of integrity required are high.

The *Guidelines* point out that in the case of loading and unloading facilities it is not possible to apply the philosophy of secondary containment.

With toxic materials even the small release which occurs as the tank is filled with a high vapour pressure

liquid may be unacceptable. In such cases use should be made of a dual transfer line system, with one line used for transfer of liquid to and from the container and the other line used for venting vapour during filling.

22.26.4 Chlorine

Guidance is given on the unloading facilities for chlorine in HS(G) 28. Some specific aspects include potential incidents, minimum separation distances, filling connections, padding gas arrangements, and systems of work.

For chlorine, flexible couplings are the normal method of connection and HS(G) 28 gives details of their use. Methods of transfer of liquid chlorine described in HS(G) 28 are the use of dry compressed air or nitrogen or of chlorine vapour, obtained by recompression or vaporization.

The system of work should ensure that one person, the driver, is present throughout the unloading, and that a second is present during connection and disconnection and is available throughout the unloading operation.

22.26.5 Ammonia

General guidance on the handling of ammonia is given in HS(G) 30, but this does not give guidance on loading and unloading facilities comparable with that for chlorine just described.

Some of the issues arising in relation to loading facilities for ammonia are discussed by Lichtenberg (1987): the use of meters vs scales; the use of hoses vs articulated arms; blowing off vs the use of integral blowdown systems; and loading by the driver or by plant personnel.

Articulated systems include vertical articulated arm systems and also compact horizontal articulated arm systems with integral blowdown.

22.27 Drum and Cylinder Storage

Another type of storage is storage in drums and similar containers and in cylinders. Although such storage is, in principle, very simple, the hazards are not trivial.

HSE guidance on drum and cylinder storage is given in CS 4 *The Keeping of LPG in Cylinders and Similar Containers* (1986), HS(G) 40 *Chlorine from Drums and Cylinders* (1987) and HS(G) 51 *The Storage of Flammable Liquids in Containers* (1990). Another relevant code is *Storage of Full and Empty LPG Cylinders and Cartridges* (LPGA, 1967 Code 7).

22.27.1 Drum storage

Chemicals are stored in containers at supplier and user sites in the chemical industry and at depot and warehouse sites.

For flammable substances guidance is given in HS(G) 51. This supersedes earlier guidance given both in CS 2 and a Home Office code. HS(G) 51 does not cover reactive chemicals such as organic peroxides, LPG or large containers.

The containers considered in this guidance include drums, portable tanks and tank containers. Reference is made to containers of 200 l. A typical container in the UK is the standard 40 UKgal drum.

Relevant British Standards on container construction are BS 814: 1974– for steel drums and BS 3951: Part 2: 1978– for freight containers.

The general approach to drum storage is broadly as follows. The preferred option is storage in the open. The storage should be in a defined area which should have an impervious surface and should be provided with a low bund or a drain and sump system. Where use is made of a bund, it is typically 150 mm high and should be large enough to hold 110% of the contents of the largest container. Within the storage area the drums should be stored in stacks which should be marked off. The stacks should have good access and ventilation. There should be separation distances between occupied buildings, the boundary, process units, flammable liquid tanks and fixed ignition sources. There should also be a maximum stack size. Guidance is given on maximum stack sizes and minimum separation distances to the objects mentioned and to LPG storage. The area around the storage should be free of combustibles and tidy. The area should be fenced off, with one or two access gates, depending on the size of the site. The storage should have a hazardous area classification as a Zone 2 area. Fire-fighting facilities should be provided. If there is difficulty in providing the separation distances recommended, some relaxation may be obtained by the provision of fire walls or fixed water sprays systems.

Alternatively, storage may be in a separate building dedicated to that purpose or in a building used also for other purposes. The latter case requires additional fire resistant construction, particularly fire walls. A building used for such storage is essentially a warehouse, to which consideration is given in the next section.

Further guidance on drum storage is given by two anonymous authors (Anon., 1979 LPB 27, p. 68); Anon. (1979 LPB 28, p. 115).

22.27.2 Cylinder storage

As for other containers, chemicals are stored in containers at supplier and user sites in the chemical industry and at depot and warehouse sites.

For LPG guidance is given in CS4. The basic principles are essentially the same as for drum storage, but there are differences of detail such as in the specific values of maximum stack size and minimum separation distances.

22.28 Warehouses

Warehouses constitute a quite different kind of storage. A wide variety of materials is stored in warehouses in many different forms. Material may be simply stored in a stockpile on the warehouse floor, but more often there are bays which hold discrete items such as paper, drums and spare parts. Chemicals in packages and drums are also stored in warehouses.

The Dangerous Substances (Notification and Marking of Sites) Regulations 1990 (the NMS Regulations) create a requirement for the notification and marking of sites which has particular relevance to warehouses. Guidance is given in HS(R) 29 *Notification and Marking of Sites. The Dangerous Substances (Notification and Marking of Sites) Regulations 1990* (HSE, 1990).

HSE guidance on warehouses is given in HS(G) 51 *The Storage of Flammable Liquids in Containers* (1990),

HS(G) 64 *Assessment of Fire Hazards from Solid Materials and the Precautions Required for their Safe Storage and Use* (1991) and HS(G) 71 *Storage of Packed Dangerous Substances* (1992). Further guidance is provided in *Guidelines for Safe Warehousing* by the CIA (1990 RC28) (the CIA *Warehouse Guide*).

Also relevant are NFPA 231: 1990 *General Storage* and NFPA 231C: 1991 *Racked Storage of Materials*.

22.28.1 Regulatory requirements

Sites which store large inventories of hazardous substances are covered by the NIHHS Regulations 1982 and CIMAH Regulations 1984. These regulations do not, however, apply to most warehouses. In a typical warehouse the quantity of any given chemical is below the threshold quantities which trigger these regulations. The necessity for the control of warehouses, however, has been highlighted by a number of incidents. The NMS Regulations 1990 were brought in to close this loophole.

In particular, the regulations are intended to provide the fire services with information to assist them in setting priorities for the inspection of sites and to warn firefighters arriving at an incident of the presence of dangerous substances.

Regulation 4 defines dangerous substances as those listed in Part 1A2 of the Approved List of the CPL Regulations 1984 and other substances with the characteristic properties set out in Schedule 2, Part 1, of those regulations. Notification is required if the warehouse stores a total of 25 te or more of dangerous substances. Regulation 5 gives requirements for access marking and Regulation 6 requirements for location marking.

There are a number of other pieces of legislation which are relevant to warehouses. In addition to those already mentioned, they include the Petroleum (Consolidation) Act 1928 (P(C)A), the Fire Precautions Act 1971, the Highly Flammable Liquids and Liquefied Petroleum Gases Regulations 1972 (HFLR), the Safety Signs Regulations 1980, the Control of Pesticides Regulations 1986, the Control of Substances Hazardous to Health Regulations 1988 (COSHH) and the current Building Regulations.

22.28.2 Management system

For the most part the companies which operate warehouses handling chemicals are not in the mainstream of the chemical industry and its culture. The operation of a chemical warehouse nevertheless demands a management system essentially similar to that in the industry.

Specifically, the management system should ensure that among other things there are formal systems which cover the identification, assessment and control of hazards; the use of suitable buildings; the storage and segregation of chemicals; the provision and maintenance of fire protection; and the use of and training in suitable operating procedures.

The responsibilities of those involved in warehouse operation are outlined in the CIA *Warehouse Code*, which covers the supplier or owner of the goods, the warehouse keeper, the warehouse supervisor and the warehouse employee.

An essential aspect of the management system is good communications.

22.28.3 Warehouse siting and layout

The siting of warehouses is often far from ideal. Many existing warehouses are located in a built-up area and close to housing. Siting of new warehouses should be such as to minimize the risks to the surrounding area. Likewise, these risks should be taken into account when considering an extension to an existing warehouse. Fire and explosion are the events which are most likely to present a threat to the surrounding population.

Many warehouses are located on waterways where they serve as transit points. This increases the risk of pollution of these waterways by chemicals released during an incident.

The layout of the warehouse site should be such as to facilitate the movement of vehicles that are unloading or loading, with adequate access and parking. The layout should aim to minimize collisions and to allow incidents such as spillages or small fires to be readily dealt with.

The layout should also assist security. Access should be gained only through access gates. Each separate warehouse building should be capable of being securely locked.

22.28.4 Warehouse buildings

The construction of a warehouse building is subject to the Building Regulations. For industrial storage buildings there is an approved document which sets out standards for compartment size and fire resistance.

Some high fire hazard substances require separation distances between the building and the boundaries in excess of those specified in the Building Regulations. These include flammable liquids, oxidizing substances and organic peroxides.

A warehouse for dangerous substances should preferably be constructed in non-combustible materials. Where flammable substances are involved there may be specific regulatory requirements for fire resistance.

Guidance on warehouse building construction is given in the CIA *Warehouse Guide*. This guidance is intended to illustrate the approach which might be taken by a chemical company in constructing a new facility. The code deals with (1) frame, (2) infill, (3) floors, (4) roof, (5) ventilation, (6) drainage, (7) emergency exit doors, (8) internal doors, (9) internal partitions, (10) wall and roof linings, (11) fire protection, (12) special facilities, (13) lighting and (14) electrical installations.

Where the dangerous substances stored are liquids, floors should be impervious and resistant to the liquid. There should be bunds to contain the liquid and sills to prevent its spread through doorways. In areas where the risk of spillage is high, there should be a separate drainage system with sloped floor, a bund and a collection sump.

Rainwater should be taken away from the roof and outside areas in drains with roof downpipes sealed at ground level. The drainage arrangements should aim to prevent contamination of surface water by water used in fighting a fire in the warehouse.

22.28.5 Material identification

There should be a formal system for the identification and tracking of the dangerous substances handled. The system should be based on the classification systems for dangerous substances. Most such substances arriving on site will be marked with the conveyance labels specified

Table 22.12 *Segregation table for storage of dangerous substances in warehouses[a] (Health and Safety Executive, 1992 HS(G) 71) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

	Class 2			*Class 3*	*Class 4*			*Class 5*		*Class 6*	*Class 8*
To be read in conjunction with Appendix 1[b]	*2.1*	*2.2*	*2.3*		*4.1*	*4.2*	*4.3*	*5.1*	*5.2*		
2 Compressed gases											
2.1 Flammable	–	1	2	2	2	2	2	2	3	1	1
2.2 Non-flammable toxic	1	–	1	1	0	2	0	0	2	0	1
2.3 Toxic	2	1	–	2	1	2	1	0	2	0	1
3 Flammable liquids	2	1	2	–	1	2	2	2	3	1	1
4 Flammable solids											
4.1 Readily combustible	2	0	1	1	–	1	2	2	2	1	0
4.2 Spontaneously combustible	2	2	2	2	1	–	1	2	3	1	1
4.3 Dangerous when wet	2	0	1	2	2	1	–	1	2	0	0
5 Oxidizing substances											
5.1 Oxidizing substances	2	0	0	2	2	2	1	–	2	1	1
5.2 Organic peroxides	3	2	2	3	2	3	2	2	–	1	1
6 Toxic substances	1	0	0	1	1	1	0	1	1	–	0
8 Corrosive substances	1	1	1	1	0	1	0	1	1	0	–

[a] The table shows general recommendations for the separation or segregation of different classes of dangerous substance. The miscellaneous dangerous substances in UN Class 9 and other dangerous substances in CPL have quite varied properties and no general advice can be given regarding segregation. Advice should be obtained from the supplier.
[b] Of HS(G) 71.

Key:

0 *Separation may not be necessary,* but suppliers should be consulted about requirements for individual substances. In particular, it should be noted that some types of chemicals within the same class may react violently, generate much heat if mixed or evolve toxic fumes.

1 *'Keep apart'.* Separate packages by at least 3 m or one gangway width, whichever is the greater distance in the store room or storage compound outdoors. Materials in non-combustible packaging which are not dangerous substances and which present a low fire hazard may be stored in the 3 m space. At least this standard of separation should be provided between substances known to react together readily, if that reaction would increase the danger.

2 *'Segregate from'.* These combinations should not be kept in the same building compartment or outdoor storage compound. Compartment walls should be imperforate, of at least 30 minutes' fire-resisting construction and sufficiently durable to withstand normal wear and tear. Brick or concrete construction is recommended. An alternative is to provide separate outdoor compounds with an adequate space between them.

3 *'Isolate'.* This is used for organic peroxides, for which dedicated buildings are recommended. Alternatively, some peroxides may be stored outside in fire-resisting secure cabinets. In either case, adequate separation from other buildings and boundaries is required.

Where a particular material has the properties of more than one class, the classification giving the more onerous segregation requirements should be used.

Note: The table is to be read in conjunction with the following paragraphs from the text of HS(G) 71. Paragraphs 20 and 21 explain the logic behind the table and paragraphs 13, 15, 22 and 23 give certain caveats.

20 Often the first material ignited in a fire is not itself a dangerous substance. For this reason, stocks of combustible materials such as easily ignitable packaging should not be kept in storerooms with dangerous substances. Separate storage areas should be provided. Similarly, even small quantities of dangerous substances stored in a warehouse for general goods may seriously increase the consequences of any fire, and in particular add to the dangers for the fire brigade. Dangerous substances should preferably be stored in dedicated warehouses or compartments of warehouses which are effectively fire separated from the remainder of the building.

21 The intensity of a fire, or its rate of growth, may be increased if incompatible materials are stored together. In addition, a fire may grow and involve dangerous substances which of themselves are not combustible. In this way, toxic materials may be widely dispersed. To prevent this type of escalation a system of segregation is necessary in warehouses storing dangerous substances.

13 The conveyance labels alone do not give adequate information for all purposes associated with storage, and the supplier should normally provide at least the additional information required under the CPL supply labelling system. This includes standard risk and safety phrases. In most cases, drivers making deliveries of a dangerous substance are required to carry on the vehicle information about the hazards of the substance(s) being carried. This may be useful if safety data sheets are not already held for substances being delivered.

15 On arrival, the contents of each consignment or individual packages should be checked, identified and assessed against the shipment documents to verify acceptability. Dangerous substances should usually be identifiable by the conveyance labelling attached to the outer layer(s) of the packaging, and for most purposes can be assessed accordingly. The additional information obtained from the suppliers may identify specific examples of non-compatibility, and storage location should take account of this.

22 The table overleaf gives recommendations for the segregation of dangerous substances of different types. The classification scheme is based on the conveyance labelling requirements of the CPL Regulations, and is consistent with the United Nations *Recommendations on the Transport of Dangerous Goods.* The table excludes Classes 1, Explosives; 6.2, Infectious substances; and 7, Radioactive substances for which guidance is given elsewhere (see Appendix 3)[b].

23 Numbers in the table relate to segregation of different classes of substance on the same floor of a building. Vertical segregation between different classes of material is not acceptable unless provided by an imperforate floor/ceiling of at least 60 minutes' fire-resisting construction.

WHERE ADVICE SPECIFIC TO A PARTICULAR CLASS OF MATERIAL IS AVAILABLE THIS SHOULD BE FOLLOWED IN PREFERENCE TO THE TABLE ABOVE.

in the Chemical Hazard (Information and Packaging) Regulations (CHIP) and goods in international transit should be labelled with the United Nations labels. The supplier should normally provide in addition the information required under the CHIP supply labelling system.

Some substances may require special storage conditions. These should be identified in advance by the supplier and accepted only if these conditions can be provided. Some substances may degrade or become unstable during prolonged storage. These too should be identified by the supplier.

All dangerous substances should be identified on receipt and their storage in and transfer from the warehouse documented. The documentation system should ensure both that records are made and that they are held securely.

22.28.6 Material segregation

The most serious incidents occur when a small event escalates and involves large quantities of material. The main cause of this is fire. An effective means of preventing such escalation is the segregation of materials.

One purpose of segregation is to separate dangerous substances from materials which may ignite or burn readily in the early stages of a fire. Another is to keep dangerous substances out of general storage where their presence is liable to aggravate the difficulties of firefighters.

Table 22.12 is the segregation table given in HS(G) 71. It is based on the conveyance labelling requirements of the CPL Regulations and is compatible with the UN *Recommendations for the Transport of Dangerous Goods.* The table does not include Class 1, Explosives, Class 6.2, Infectious Substances, or Class 7, Radioactive Substances, which are covered by separate guidance. The numbers in the table refer to the segregation of different classes of substance on the same floor of a building. Vertical segregation between different classes of material is not accepted except where there is an imperforate floor/ceiling with 1 hour fire resistance. The general guidance given in the table is overridden where there is advice specific to a particular class of material.

The *International Maritime Dangerous Goods Code* may also be used as guidance, provided allowance is made for the different factors which apply to land storage.

22.28.7 Mechanical handling

Modern warehouses make full use of mechanical handling aids. There is also a trend towards automated warehouses under computer control. The mechanical handling facilities should accommodate the full range of packages to be stored, so that improvization is avoided.

Widespread use is made in warehouses of pallets and forklift trucks. Guidance on the use of forklift trucks is available (HSE, 1992 HS(G) 6). Forklift trucks are also considered in Chapter 21.

22.28.8 Storage operation

There are a number of basic operating principles which should be covered by formal operating procedures.

When a consignment is received, the substance should be identified and the integrity of the package should be checked. Damaged packages should not be accepted into store but dealt with by repacking or disposal.

Each location should have a specified storage capacity which should be adhered to. There should be maximum stack sizes and heights. The heights should take into account the potential for damage to the packages at the bottom and for fire spread. The racking used should be well constructed and should not be overloaded. Goods should not be stored so close to a wall as to interfere with ventilation or in gangways so that they inhibit access.

Stock held for a prolonged period should be inspected for degradation. Where a substance has a maximum storage time this should not be exceeded. If this is close to occurring, the advice of the manufacturer should be sought.

There should be arrangements for dealing with spillages. This is partly a matter of building design, as already described, but it is also necessary to provide an absorbent and to have procedures for dealing with and disposing of the spillage.

Where appropriate, an operation should be governed by a permit-to-work.

22.28.9 Fire protection

The fire potential in a warehouse is high. The fire load is very high and the conditions for fire spread are nearly ideal, there being large amounts of combustibles close together and with good air circulation. In fact a large proportion of fire loss in storage is due to warehouse

fires. The prevention of fires in warehouses is therefore extremely important.

Fire protection in warehouses includes the following measures: (1) building construction, (2) control of ignition sources, (3) fire detection systems, (4) fire protection systems, and (5) operational measures.

As already stated, the building should preferably be constructed in non-combustible materials and have a degree of fire resistance. The starting point is a concrete or steel frame. Other aspects of fire resistant construction are concrete protection of the steel supporting columns, separation of the arrival and dispatch areas from the storage area by fire resistant walls, and further separation by fire resistant walls within the storage area.

Whereas in process plant handling flammables the first line of defence is to remove the fuel by keeping the flammable material contained, in a warehouse storing flammable substances the fuel is to hand. Hence close control needs to be exercised over ignition sources.

The warehouse should be covered by hazardous area classification. Normally the appropriate classification is Zone 2 and the arrangements should then be such that no operation requires a more stringent classification.

Forklift trucks are a particular potential ignition source which require control. Where a hazardous area classification applies, only trucks suitable for use in that area should be used.

Fire detection systems are valuable in giving rapid warning of a fire. Whether detection is followed first by warning to personnel and manual fire fighting methods or by immediate activation of automatic fire protection systems such as sprinklers depends on the circumstances. Problems with the latter include false alarms and water damage.

Sprinklers are the principal form of fire protection device used and are generally effective. For high warehouses sprinklers on the roof may be insufficient and they may need to be provided at lower levels as well. Sprinkler protection is discussed further in Chapter 16.

There should be a working discipline, essentially similar to that required in a process plant, which ensures that procedures are observed. These include general good housekeeping, the avoidance of obstructions to corridors and fire doors, and the elimination of ignition sources.

The HSE has developed a test, described in HS(G) 64 (HSE, 1991) and referred to as the HSE Test, which may be used to assess the need for particular forms of fire protection. Details of the test are given by Wharton (1990). The test characterizes a material in terms of (1) the maximum rate of vent temperature rise and (2) the total smoke evolution. For each of these two features the material is placed in one of two hazard categories according to the following scheme:

Category	*Temperature rise* (°C/min)	*Smoke* (m^3 ODml)
HIGH	≥700	≥400
NORMAL	<700	<400

[a] OD, optical density – see Wharton (1990)

In some cases it may be a condition of a fire certificate under the FPA (1971) that certain precautions be taken for the storage of a HIGH fire hazard material. In any event it is desirable that a HIGH fire hazard material should be stored in a separate area, either in a separate building, a single storey extension of the main building or in the open air. Where it is not reasonably practicable to store such a material elsewhere than in the main building, it should be stored in an area separated from the rest of the building by a 30 minute fire partition. A HIGH fire hazard material should not be stored in a basement or below an occupied floor. Exceptions to this are given in HS(G) 64 such as cases where the quantities are small or the risk is reduced by the type of packaging used or by some combination of spacing and active fire protection.

The problem of fire protection in warehouses is complex. The discussion of the problem, in relation to automated high bay warehouses, by the FPA (1970/9) outlines some of the difficulties.

Arson is a potential problem in warehouses. Guidance from the FPA also includes a treatment of the prevention and control of arson (1992 AR2).

22.28.10 Hazard assessment

Substances stored in warehouses may be hazardous by virtue of their being combustible, flammable, explosive, toxic, corrosive, unstable, reactive with air and/or water, pyrophoric or liable to spontaneous combustion or oxidizing.

There should be a system for the identification of the hazards. A checklist approach may in large part fulfil this function.

A hazard assessment should be performed, broadly on the lines of those made for process plant, but allowing for the characteristic features of warehouses. Initiating events may be associated with: liquid spillage due to leaks or the opening of valves; spillages of solid materials due to damage to packages or to repackaging operations; dust clouds; or small fires. Scenarios of escalation may include a major fire, a series of explosions, a release of toxic gases and vapour within the warehouse or beyond, a large smoke cloud (possible highly toxic) or the overflow of large quantities of contaminated fire water.

22.28.11 Emergency planning

There should be an emergency plan for the warehouse, adapting the basic principles described in Chapter 24 to warehouse conditions. The plan should be suited to the level of the assessed risk and should be developed in consultation with the local emergency services. Personnel should be trained in the plan and in their own role in it, and exercises should be conducted.

22.29 Warehouses: Particular Chemicals Storage

There are certain chemicals which are stored in warehouses that merit particular consideration.

22.29.1 Sodium chlorate

Sodium chlorate is a crystalline solid which is relatively stable and is a strong oxidant. It has a melting point of 248°C and starts to decompose at 265°C with the evolution of oxygen.

Guidance on the storage of sodium chlorate is given in CS 3 *Storage and Handling of Sodium Chlorate and Other Similar Strong Oxidants* (HSE, 1985). This guidance also applies to the several other strong oxidants listed.

There have been several warehouse fires, two of which are described below, in which the involvement of sodium chlorate has resulted in violent explosions.

One hazard of sodium chlorate is that it may become involved in a fire and explode, as just described. Another is that it may become mixed with a readily oxidizable material, such as a fuel. Such a mixture can be ignited by relatively mild stimuli and can burn with explosive violence.

Sodium chlorate should be stored in a secure and separate area. It should be segregated from combustible materials and contaminants should be excluded. Control should be exercised over ignition sources and measures should be taken to prevent the material becoming involved in a fire.

Storage for sodium chlorate may be in the open on a concrete pad, with or without a roof, but should preferably be fully enclosed. Any structure should be built of non-combustible materials and the floor should be smooth, impervious and non-carbonaceous. CS 3 gives maximum stack sizes and minimum separation distances for the storage of sodium chlorate.

Packaging of sodium chlorate is preferably in metal drums with a plastic liner. International agreements on transport also authorize the use of certain soft packaging materials such as flexible intermediate bulk containers.

Wooden pallets should not be used for the routine handling of sodium chlorate as they are liable to become impregnated with it, thus creating a fuel–oxidant mixture. CS 3 advises, however, that where wooden pallets do form an integral part of an IMO *Code* approved package and the wood is new, they may be allowed for one-off storage.

In view of the fact that the fires in the two warehouse incidents described in Section 22.30.7 were caused by outsiders, security assumes particular importance in the storage of sodium chlorate.

22.29.2 Organic peroxides

Organic peroxides are highly reactive and thermally unstable substances which undergo self-accelerating decomposition. They have oxidizing properties and some are also toxic.

Guidance on the storage of organic peroxides is given in CS 21 *Storage and Handling of Organic Peroxides* (HSE, 1991)

In the pure state some organic peroxides detonate. For commercial use organic peroxides are desensitized, but even so they are capable of runaway decomposition. Such decomposition may be caused by heating or contamination.

The self-accelerating decomposition temperature (SADT) of an organic peroxide is determined by test. The SADT tends to decrease with package size. A control temperature is specified which is the maximum storage temperature, and an emergency temperature at which emergency procedures should be implemented. The relationships between these two temperatures and the SADT are given in CS 3. Another aspect of temperature control is that in some cases an organic peroxide can separate out of solution if cooled, resulting in a concentrated peroxide which may be shock sensitive.

Organic peroxides should be stored in the original containers in a dedicated storage and segregated from other materials. They should be maintained within the specified temperature limits. Contaminants should be excluded.

Further detailed guidance on the storage of organic peroxides is given in CS 3. They are classified into four flammability types, Types 1–4. A distinction is made between storages up to 150 kg and above 150 kg. Minimum separation distances are given. A list is given of packaged organic peroxides by flammability type.

22.29.3 Ammonium nitrate

Ammonium nitrate (AN) is a crystalline solid with a melting point of 170°C which decomposes above 210°C. Most of the commercial material stored is some form of mixture.

Guidance on the storage of AN is given in CS 18 *Storage and Handling of Ammonium Nitrate* (HSE, 1986).

AN is an oxidizing agent. It is not itself combustible, but it can assist the combustion of other materials, even if air is excluded. It is insensitive to the friction and impact of normal handling, but it can be detonated under conditions of heat and confinement or by severe shock. The probability of explosion is much increased if the AN is mixed with organic matter. In a fire, molten AN may form and flow into areas, such as drains, where it becomes confined and/or contaminated, and it may then explode. Furthermore, when heated in a fire, AN gives off toxic fumes, mainly oxides of nitrogen.

The main requirements in the storage of AN are to avoid heating or involvement in a fire, serious confinement, and contamination.

CS 18 makes a distinction between AN and AN fertilizers with $\leq$28% nitrogen and those with $>$28% nitrogen. It deals mainly with the latter.

Storage of AN with $>$28% nitrogen should be in a dedicated building constructed in materials which are not readily combustible and with good ventilation or in the open on a concrete pad. Measures should be taken to avoid the hazard of molten AN becoming confined or contaminated, particularly in drains.

AN in storage should be segregated from other materials. The storage should be located away from potential sources of heat, fire or explosion, including combustible and flammable materials. CS 18 gives maximum stack sizes and minimum separation distances.

Packaging of ammonium nitrate is typically in 50 kg bags of material impermeable to oil or water. Paper packaging should not be used. The bags should preferably be palletized. If wooden pallets are used, they should be uncontaminated.

With regard to AN fertilizers with $\leq$28%N, whilst most are not combustible, a few are capable of self-sustaining decomposition with strong evolution of toxic fumes. These are known as 'cigar burners'.

AN storage should be provided with good security. CS 18 states that access should be prevented not only of unauthorized persons but also of animals. Whilst it does not elaborate, the point is presumably that an animal may not only damage packaging but may leave behind organic material.

22.30 Storage Case Histories

22.30.1 Oil storage

In the storage of petroleum products there have been numerous cases of tank overpressure or vacuum collapse and of fire, and some cases of release from tanks.

A review of the failure of storage tanks containing oil and similar products has been given by Wilkinson (1991 SRD R530). He divides the incidents into mechanical and brittle fracture failures and failures following an explosion or bund fire.

On 30 August 1983, a fire started on the floating roof of an oil storage tank at a refinery at Milford Haven, Wales (Case History A106). The tank contained some 47 000 ton of light crude oils. There were fine cracks in the floating roof through which oil had seeped out. It is believed to have been ignited by hot carbon particles from the flare. The fire was massive, with three boilovers of burning oil. It was not extinguished until 2 days later.

On 2 January 1988, at Floreffe, Pennsylvania, a storage tank containing diesel oil suffered a sudden collapse (Case History A120). The tank split vertically and the force of the oil spurting out moved the tank 100 ft off its foundations. The tank cracked, collapsed and crumpled. A proportion of the oil flowed over the bund and entered the waterways. The tank had been reassembled after removal from another site and the failure occurred on its first filling after reassembly.

22.30.2 LPG storage

A review of LPG storage incidents has been given by Davenport (1986), who describes incidents at: Port Newark, New Jersey, on 7 July 1951; Feyzin, France, on 4 January 1966; Texas City, Texas, on 30 May 1978; and Mexico City, Mexico, on 19 November 1984. Accounts of these incidents are given in Case Histories A19, A38, A92 and in Appendix 4, respectively.

The Port Newark site had $100 \times 115\ m^3$ horizontal pressure vessels for propane, in two groups, one of 70 vessels and the other of 30 vessels, separated by a distance of 106 m. A leak of unknown origin occurred in pipework near the vessels in the larger group. Within a few minutes the first vessel burst. Eventually all 70 tanks in the group ruptured with varying degrees of violence. None of the vessels in the smaller group failed.

At Feyzin there were four $1200\ m^3$ propane and four $2000\ m^3$ butane pressure storage spheres. An escape of liquid propane occurred whilst water was being drained from the bottom of one of the propane spheres. The vapour cloud formed was ignited by a vehicle on a nearby road and the vapour cloud fire caused a series of BLEVEs which resulted in 18 deaths and the destruction of five of the spheres.

At both Texas City and Mexico City the initiating event is believed to have been overpressure of a vessel which was being filled from a pipeline. At Texas City there were three pressure storage spheres and a number of other pressure vessels. The hypothesis is that the sphere which was overpressured developed a crack and released material which found a source of ignition. It was reported that the vapour cloud fire then changed to a jet flame at the sphere. Within a short time the sphere failed, giving a huge fireball. This was followed by a series of explosions and fires, and the failure of the other two spheres.

The site at Mexico City contained four $1600\ m^3$ and two $2400\ m^3$ pressure storage spheres and 48 horizontal cylindrical pressure vessels for storing propane and butane. The leak gave rise to a vapour cloud which ignited at a neighbouring plant and, within a short time, one or possibly two of the spheres ruptured. There followed a series of explosions and fires, which killed some 500 people and destroyed many of the storage vessels.

Another significant incident is that of a 260 000 bbl refrigerated LPG tank at Umm Said, Qatar, on 3 April 1977 (Case History A88). A massive failure occurred and a wave of liquid propane swept over the bunds and inundated the process area of the associated NGL plant before igniting. The NGL plant was completely destroyed.

22.30.3 LNG storage

One of the earliest process industry disasters was the failure on 20 October 1944 of an LNG storage tank at Cleveland, Ohio (Case History A12). The cause of the rupture is believed to have been the use of a low carbon steel which was unsuitable for the low temperatures involved. A vapour cloud of LNG formed and ignited in the plant itself, whilst LNG liquid flowed into storm sewers, where it mixed with air and gave rise to a series of explosions. Some 128 people were killed.

A quite different case is the disaster at Staten Island, New York, in 1973 (Case History A67). Work was being done inside an empty LNG storage tank when flammable residues were ignited. Some 40 people died in the resultant fire.

A rollover incident occurred on 21 August 1971 at the SNAM LNG terminal at La Spezia in Italy (Case History A54). A sudden increase in pressure occurred in the tank, causing a discharge from the tank safety valves and tank vent. The release from the safety valves lasted for 75 minutes and that from the vent lasted 3 hours and 15 minutes.

22.30.4 Ammonia storage

A review of the failure of ammonia storage failures has been given by Markham (1987b). He presents information on the ammonia concentrations as a function of distance in these incidents and on the physiological effects of ammonia on humans, animals and plants.

On 13 July 1973, a sudden failure occurred on a horizontal ammonia pressure storage vessel at Potchefstroom, South Africa (Case History A65). The cause of the failure was brittle fracture of the dished end. The ammonia spread as a dense gas cloud over the works and to an adjacent township. Eighteen people were killed.

On 16 November 1970, a 40 000 ton refrigerated atmospheric ammonia tank at Blair, Nebraska, was overfilled (Case History A47). The ammonia overflowed and formed a massive dense gas cloud which extended some 9000 ft. The area was sparsely populated and no-one was killed.

In 1982, defects were observed on a 20 000 te refrigerated atmospheric ammonia tank at Arzew, Algeria (Martinez *et al.*, 1987). They included tilting, extensive degradation of the tank wall insulation and

failures of the anchor bolts. The cause is not known, but two hypotheses were advanced. One is an earthquake—there were earthquakes nearby in 1980 and 1981. The other is frost heave, due to poor drainage, with the resultant accumulation of water in the aeration tubes and hence a reduction in the efficiency of the foundation heating.

On 2 October 1984, a 15 000 ton refrigerated ammonia storage tank at Geismar, Louisiana, suffered a catastrophic failure of the roof-wall weld two-thirds of the way around its circumference (Badame, 1986). There was some release of ammonia which gave a small cloud, but evidently had no serious consequences. The tank had suffered a mild overpressure of some 0.5 psi. The refrigeration compressors were down at the time. The relief valve opened but did not have the capacity to prevent the pressure from increasing. The weld had been subjected over the 17 years of the tank life to some 80 000 cycles and was held to have failed due to low cycle fatigue. It also showed extreme lack of penetration.

Another refrigerated atmospheric ammonia tank failure occurred on 20 March 1989 at Jonova, Lithuania (Case History A124). Some warm ammonia had been charged to the tank and in due course it erupted, causing a sudden increase in pressure. A massive failure occurred between the wall and the bottom of the tank and liquid ammonia rushed out. At the same time the tank was dislodged from its foundations and smashed violently through the containing wall on the far side from the escape, ending up 40 m away. A pool of liquid ammonia formed which in places was 70 cm deep. The ammonia suddenly ignited and the whole plant area was engulfed in flames. A burning conveyor belt transmitted the fire to a store of NPK fertilizer. Seven people were killed.

22.30.5 Pressure storage vessels

In 1986 a pressure storage vessel holding 25 te of carbon dioxide ruptured (Coleman, 1989). The report on the failure concluded that the steel was brittle at its service temperature and that inadequate leg attachments had created high local stress. The metallurgical evidence indicated that the heat treatment had not been properly carried out. There was also doubt whether the steel used in fabrication was the same as that on which the impact tests required had been performed.

22.30.6 Pressure storage vessels: decommissioning

Accounts of the decommissioning of pressure storage vessels also merit mention, even though in these cases no release occurred.

Squire (1991) records the case of an ammonia pressure storage vessel as follows:

> A bullet tank in refrigeration service had been cleverly made by turning a high-pressure distillation column on its side. While possessing considerable strength at ambient temperature, subsequent analysis showed no strength (< 2 ft-lb) at 0°C. The bullet was immediately removed from service after identification. Great care was taken during the deinventory so as not to fracture the vessel.

Coleman (1989) describes an investigation into the state of a set of pressure vessels for the storage of carbon dioxide. The investigation was prompted by the carbon dioxide storage vessel failure just described. The company commissioned an investigation of its other carbon dioxide storage vessels, of which there were 24 vessels ranging in age from brand new to 26 years old. The work addressed in particular the risk of brittle fracture, and the methods used included visual examination, replica metallurgy and ultrasonic testing. The result of the investigation was that three vessels were taken out of service because it was found that their dished ends had been overheated during hot forming. Suspect metallurgy led to the withdrawal of a further six vessels, five of which had not only low toughness but also problems such as laminations and inclusions, weld defects and directly attached support brackets. All but one of these vessels were built before 1970, and most dated from before 1965.

22.30.7 Warehouses

On 4 January 1977, a serious fire and explosion destroyed a chemicals warehouse and adjacent whisky warehouse at Braehead and resulted in widespread window and roof damage within a 1 mile radius (Case History A85). Subsequent experimental investigation showed that explosions of this severity can be caused by the involvement of sodium chlorate under intense heat conditions. The warehouse had contained some 67 te of sodium chlorate in steel drums. The fire was started by boys who had built a 'den' beside the warehouse and had lit a fire there to warm themselves.

On 25 September 1982, a fire, followed almost immediately by an explosion, occurred in the warehouse of B&R Hauliers at Salford (HSE, 1983b) (see also Case History A85). The warehouse contained some 2000 te of chemicals, including 25 te of sodium chlorate. There was evidence that the original fire had been started outside the building by vandals and also that, earlier, persons had entered the warehouse where various containers were opened and chemicals mixed. The management had been unaware of the guidance issued by the HSE on sodium chlorate.

Another warehouse incident which involved a much smaller amount of sodium chlorate, some 2.45 te, but which nevertheless proved serious enough, occurred on 21 January 1980 at Barking, Essex (HSE, 1980a) (see also Case History A85). A fire started, probably caused by a domestic bar fire, possibly drying wet clothing, and spread through packaging materials to involve various chemicals. There were three explosions, probably one was of an LPG cylinder and the other two of sodium chlorate. Nine firemen were injured.

22.31 Storage Risk

22.31.1 Historical record

The risks from the process industries arise from processes, storage and transport. The historical record shows that storage is a major contributor. Storage figures prominently in the case histories given in Appendix 1 and elsewhere in this book. An attempt to quantify the contribution made by storage to the overall risks from the process industries is given below.

22.31.2 Hazard assessment

Another approach to the estimation of the risks from storage is hazard assessment. Two major hazard assessment exercises in which storage figures prominently are

the *Canvey Report* and the *Rijnmond Report*, which are described in Appendices 7 and 8, respectively.

An account is given below of hazard assessments of the storage of the principal hazardous substances: LPG, LNG and ammonia.

22.31.3 Storage vs process

Although the quantities of hazardous materials held in storage are much larger than in process, it is usually considered that process is the principal hazard. This view is reflected in the distinction made in the EEC Directive on Major Accident hazards between process and process associated storage on the one hand, and isolated storage on the other.

A study of the relative risks from process and storage has been made by Lees (1983d). He considered the following three principal sets of data:

(1) accidents involving 10 or more deaths;
(2) accidents involving 2 to 9 deaths;
(3) fire losses.

The data used in this study are given in Tables 22.13–22.15. The accidents listed in Table 22.13 were taken from the list given in Appendix 3 of the first edition of the present book. The table shows process and storage as the source of 14 and 9 accidents, respectively, making the latter 39% of the total. Table 22.14 shows the contribution of storage, rising from 13% for accidents involving 2 deaths to 36% for accidents involving 6–9 deaths. Of the fires given in Table 22.15, 195 were in process and 23 in storage. Storage was thus the source of 11% of the fires. However, 72% of the financial loss was attributable to storage.

Lees states:

> What the foregoing data appear to indicate is that the contribution of storage to deaths in multiple fatality accidents in the oil and chemical industries tends to increase with the number of fatalities and for accidents involving 5 or more fatalities to approach a figure of the order of 20–35%. Thus the idea that material in storage presents a much lower risk than that in process is a half-truth and cannot be accepted without qualification. As far as concerns multiple fatality accidents, and in particular large multiple fatality accidents, the contribution of storage is appreciable.

Since this study the accidents at Mexico City and Bhopal have occurred, both of which involved storage.

22.32 LPG Storage Hazard Assessment

Turning now to hazard assessment of storage, treatments fall into three groups: (1) overview, (2) generic study and (3) specific study. A particular form of the second group is the guidance issued by the HSE or industry associations on safety cases.

Overviews of the hazard assessment of LPG pressure and refrigerated storage have been given in the *Canvey Reports* (HSE, 1978b, 1981a), and by Rasbash (1979/80) and Lyon, Pyman and Slater (1982). Generic hazard assessments of LPG pressure and refrigerated storage have been described by Considine, Grint and Holden

Table 22.13 *Some major accidents involving 10 or more deaths in the oil and chemical industries (Lees, 1983d) (Courtesy of Elsevier Science Publishers)*

Date	*Location*	*Deaths*	*Process/storage*
1926	St Auban	19	Storage
1928	Hamburg	10	Storage
1939	Zarnesti	c. 60	Storage
1944	Cleveland	128	Storage
1944	Denison	10	Storage
1947	Rauma	19	Storage
1950	Poza Rica	22	Process
1959	Ube	11	Process
1960	Kingsport	15	Process
1962	Toledo	10	Process
1965	Louisville	12	Process
1966	Feyzin	18	Storage
	LaSalle	11	Process
1968	GDR	24	Process
1972	Brazil	37	Storage
	Weirton	10	Process
1973	Potchefstroom	18	Storage
1974	Czechoslovakia	14	Process
	Flixborough	28	Process
1975	Beek	14	Process
	Scunthorpe	11	Process
1976	Chalmette	13	Process
1977	Columbia	30	Process

Table 22.14 *Some lesser accidents involving two to nine deaths in the oil and chemical industries (Lees, 1983d) (Courtesy of Elsevier Science Publishers)*

	No. of deaths per accident				
	2	*3*	*4*	*5*	*6–9*
Process					
No. of accidents	26	13	9	4	11
Total No. of deaths	52	39	36	20	81
Storage					
No. of accidents	4	3	3	1	5
Total No. of deaths	8	9	12	5	46
Deaths from storage (%)	13	19	25	20	36

Table 22.15 *Some fire loss data for the petroleum industry[a] (Lees, 1983d) (Courtesy of Elsevier Science Publishers)*

	No. of fires	*Frequency of fires* (fires/100 properties)	*Cost per fire* (US$)
Refineries	176	141.9	204 000
Natural gas plants	19	3.72	49 000
Tank farms	3	1.05	127 000
Bulk terminals (shore)	11	2.06	313 000
Bulk plants (inland)	9	0.97	195 000

[a] Data are for fires in 1977, as given by the API survey.

Table 22.16 *Event frequency/probability estimates given in two LPG hazard assessments (after Drysdale and David, 1979/80; Considine, Grint and Holden, 1982)*

A Pressure storage sphere: Drysdale and David

	Frequency/probability (per year)
Crack in pipe	10^{-4}/year
Gasket failure	5×10^{-5}/year
Flange failure	4×10^{-5}/year
Valve seating failure	3×10^{-2}/year
Drainage/sampling valve not properly shut	10^{-4}/year
Pipe rupture due to:	
Vehicle impact	10^{-5}/year
Vibration	10^{-2}/year
Corrosion	10^{-4}/year
Repair whilst operating	10^{-4}/year
Excess pressure (blockage)	10^{-7}/year
Fatigue	10^{-4}/year
Creep	10^{-5}/year
Sabotage	2×10^{-3}/year
During filling operation:	
Operator fails to stop filling when correct level is reached	0.1
Operator fails to stop pump quickly enough when release occurs	10^{-2}
Fixed water spray inoperative because:	
Water shut off	10^{-2}
Activation fails	2×10^{-2}
Water frozen	5×10^{-4}
Pipes completely blocked	10^{-4}
Low main pressure	3×10^{-3}
Sprinkler system damaged	10^{-5}
Fixed water spray system ineffective because:	
Pipes partially blocked	3×10^{-4}
Low mains pressure	2×10^{-3}
Some heads blocked	8×10^{-4}

B Pressure storage: Considine, Grint and Holden

Event	*Frequency*[a]*/probability*	*Flow*[b]
Catastrophic failure of vessel:		
Complete failure	3×10^{-6}/vessel-year	Instantaneous release of 1500, 2250 or 3000 te
Failure equivalent to 6 in. nozzle	7×10^{-6}/ vessel-year	15 te/min
Fracture of 6 in. liquid line[b]		1 te, or 1 te + 50 kg/s
Pipework	3×10^{-7}/m-year	
Equivalent failure of fittings	5×10^{-6}/item-year	
Release due to overfilling[c]	10^{-4}/vessel-year	30 kg/s
Fracture of 2 in. vapour line	3×10^{-6}/m-year	1 kg/s
Serious leak from equipment or pipework (1 kg/s):		
6 in. pipework	6×10^{-6}/m-year	
2 in. pipework	6×10^{-5}/m-year	
Flange	3×10^{-4}/flange-year	
Pump seal	5×10^{-3}/seal-year	
Release in course of draining or sampling (1.5 kg/s):		
Release per operation	10^{-4}	
Draining operations	50/year	
Sampling operations	100/year	
Failure to recover during draining	10^{-1}	
Failure to recover during sampling	10^{-2}	

C Refrigerated atmospheric storage: Considine, Grint and Holden

Event	*Frequency*[a]	*Flow*[b]
Catastrophic failure of tank	5×10^{-6}/tank-year	Instantaneous release of 1500, 2250 or 3000 te
Rollover[e]	10^{-5}/tank-year	Instantaneous release of 1500, 2250 or 3000 te
Overfilling[d, f], of which:	10^{-4}/tank-year	
With tank failure[e]	10^{-5}/tank-year	Instantaneous release of 1500, 2250 or 3000 te
Without tank failure	9×10^{-5}/year	50 kg/s
Fracture of 6 in. liquid line	As Section B	50 kg/s
Leak from pipework, etc.	As Section B	1 kg/s

[a] Basic frequencies for a single vessel or tank.
[b] The flows given are complex; quantities quoted here are specimen values and in some cases are not sustained for more than 1 minute.
[c] Probability of emergency shut-off failure 0.2.
[d] Based on protective system design.
[e] Probability of wall-base failure 0.25; probability of wall-roof failure 0.75.
[f] Probability that operator switches off pump and limits the event to a release into the bund rather than tank failure, 0.9.

(1982) and of pressure storage by Drysdale and David (1979/80), T.A. Smith (1985), Crossthwaite (1984, 1986) and Clay *et al.* (1988). Guidance on safety cases for LPG has been issued by the LPGA (1989 GN1). Specific hazard assessments of LPG pressure and refrigerated storage are given in the *Canvey Reports*, and of pressure storage by Khan (1990).

The hazard assessments of LPG given in the *Canvey Reports* are described in Appendix 7 and are therefore not considered further at this point.

The hazard assessments by Crossthwaite and Clay *et al.* are part of a generic methodology for the assessment of LPG, and by extension similar flammable materials, developed by the HSE; they are described in Chapter 9.

The studies by Drysdale and David and by Considine Grint and Holden are essentially generic risk assessments, the former dealing mainly with risk to plant personnel and the latter with risk to the public.

22.32.1 Pressurized storage

The classification of initiating events and hazard scenarios for the pressure storage of liquefied gas shown in Table 22.2 is broadly applicable to LPG. For a pressure storage vessel containing LPG principal hazardous events are catastrophic failure of the vessel, a major crack on the vessel, a major leak from the associated pipework, release due to overfilling of the vessel, a jet fire and an engulfing fire.

In the hazard assessment made by Drysdale and David (1979/80), the object considered is a 600 te propane pressure storage sphere with, at the four points of the compass, open sea at a distance of 50 m, a chemical plant at 150 m, a main road at 200 m and a loading bay at 50 m. They treat the following events: (1) a crack in the vessel, (2) a small leakage from the pipework and (3) a large leakage from the pipework. They consider the scenarios of a fire at the vessel, leading to a BLEVE, a vapour cloud flash fire and a vapour cloud explosion (VCE).

The authors give fault trees for the estimation of the frequency of: a fire at the sphere due to a small leak and for one due to a large leak; a BLEVE under fire conditions; and for a VCE. Some of the event frequency and probability estimates which they use are shown in Table 22.16, Section A. Many of these estimates are judgement figures and some differ from other literature values.

For ignition they assume the following probabilities for the presence of an ignition source: at the chemical plant, 1.0; at the main road, 0.5; and at the loading bay, 0.05. They further assume that the probability of ignition by the ignition source is 0.5 in each case.

With regard to consequences, these authors make the assumption that all the propane released evaporates. They use the Gaussian passive gas model to estimate the travel distances of the resultant cloud. The principal hazardous outcomes which they consider are a BLEVE and a VCE, the other outcomes being a vapour cloud flash fire and dispersion without ignition.

They assess the risks to the public as very low, but draw attention to the appreciable risk to firefighters from a BLEVE, a risk which was realized at Feyzin.

The object assessed by Considine, Grint and Holden (1982) is one of two 1500 te butane spheres. Two sites are considered, both a 500 m square site with the storage object located at one corner. The urban site is surrounded on all sides by population at 100 m from the site and the remote site by population at a radial distance of 1000 m in all directions. They treat the following scenarios: (1) a catastrophic failure of the vessel (explosive failure), (2) a catastrophic failure (equivalent to a 6 in. nozzle), (3) a fracture of a liquid line, (4) a fracture of a vapour line, (5) overfilling, (6) a serious leak from the pipework, and (7) a leak due to a draining or sampling operation.

The authors consider the scenarios shown in Table 22.16, Section B, and give the event frequencies shown in that table.

Their model for ignition at source is as follows:

Release	*Probability of ignition*		
	Immediate	*Delayed*	
		Wind over site	*Wind not over site*
Large instantaneous	0.25	0.25	0.25
1000 te	0.25	0.25	0.1
250 kg/s, 50 kg/s	0.25	0.25	0.1
30 kg/s, 16 kg/s	0.15	0.15	0.05

The probability of ignition of a cloud reaching the edge of the populated area is taken as 0.7 and that of ignition over the populated area as 0.2.

For both for the pressure storage and refrigerated storage cases, Considine, Grint and Holden consider the following scenarios (1) immediate ignition at source, (2) delayed ignition at source, (3) ignition at the edge of the population zone, and (4) ignition over the centre of the population zone.

For pressure storage, the immediate ignition at source of an instantaneous release is assumed to give rise to a fireball, and the immediate ignition of a continuous release is assumed to give rise to a jet flame, or torch fire. If ignition is not immediate, the cloud drifts. For an instantaneous release the assumption of complete vaporization is made and the gas dispersion is modelled using the DENZ dense gas dispersion code. The method used for the dispersion of the continuous releases is unclear, but appears to be the Gaussian model. For the three cases of delayed ignition the outcomes are flash fires and VCEs.

The authors assumed that catastrophic explosive failure of one of the spheres would cause failure of the other also. Furthermore, a proportion of torch fires are capable of causing a BLEVE of a sphere. The total frequency of torch fires was assessed as 3×10^{-3}/year and that of BLEVEs as 7.1×10^{-5}/year.

Thus the principal outcomes considered are: an explosive failure, generating missiles and causing failure of the other sphere; a fireball; jet flames; a BLEVE; a vapour cloud fire; and a VCE. The authors outline the models used and the associated injury relations.

The risks estimated in this hazard assessment are given in Section 22.32.3.

It will be apparent from this description that different analysts tend to formulate scenarios in somewhat different ways, even where the events considered are similar.

22.32.2 Refrigerated storage

The classification of initiating events and hazard scenarios for the refrigerated storage of liquefied gas shown in Table 22.2 is broadly applicable to LPG.

For a refrigerated storage tank containing LPG the principal hazardous events are catastrophic failure of the tank, explosion in the vapour space of the tank, rollover, a major leak from the associated pipework and release due to overfilling of the tank.

The object assessed by Considine, Grint and Holden (1982) is a single refrigerated atmospheric fixed roof, single-wall storage tank containing butane positioned at the same location as the two pressure storage spheres already described. They treat the following events: (1) catastrophic failure of the tank, (2) rollover, (3) overfilling, (4) a fracture of a liquid line and (5) a leak from the pipework.

The authors consider the scenarios shown in Table 22.16, Section C, and give the event frequencies shown in that table. They use the same ignition model as for the releases from pressure storage.

As for the pressure storage case they consider the four cases of immediate ignition at the source and of delayed ignitions at the source, at the edge of and over the population zone.

For instantaneous release by catastrophic failure of the refrigerated storage tank, Considine, Grint and Holden take into account overtopping of the bund. Immediate ignition of an instantaneous release is assumed to give a pool fire. If ignition is not immediate, vaporization occurs, which the authors estimate using the SPILL code. Immediate ignition of a continuous release is evidently also assumed to result in a pool fire. The dispersion of releases which are not immediately ignited at source is modelled using the same method as for the pressure storage study. Outcomes of delayed ignition of these releases are pool fires, torch fires, vapour cloud flash fires and VCEs.

Further principal sources of information on the frequency or probability of events, on consequences and on assessed risk for LPG storage are the *Canvey Reports* and the *Rijnmond Report.*

22.32.3 Pressurized vs refrigerated storage

The study conducted by Considine, Grint and Holden was primarily directed at the comparison of the risks arising from the two types of butane storage in the two types of location. The comparative risks assessed by these authors for the specific configurations considered are:

Site	*Storage*	*Individual risk* ($\times10^{-6}$ year^{-1})	*Societal risk (casualties > N)* ($\times10^{-6}$ year^{-1})			
			>10	>100	>1000	>5000
Urban	Pressurized	102	159	84	76	40
	Refrigerated	35	66	7.1	7.0	1.6
Rural	Pressurized	12	76	76	76	36
	Refrigerated	0.26	2.0	2.0	0.08	–

22.33 LNG Storage Hazard Assessment

Overviews of the hazard assessment of refrigerated LNG storage have been given in the two *Canvey Reports* (HSE, 1978b, 1981a) and the *Rijnmond Report* (Rijnmond Public Authority, 1982) and by Kopecek (1977), R.A. Cox, Comer *et al.* (1980), Philipson (1980), Kunreuther and Lathrop (1981), Lyon, Pyman and Slater (1982), Nassopoules (1982), Philipson and Napadensky (1982), Valckenaers (1983), Wicks (1983), D.A. Jones (1985), Valk and Sylvester-Evans (1985), Napier and Roopchand (1986), D.F. Cooper and Chapman (1987) and Navaz (1987). Specific hazard assessments of LNG refrigerated storage are given in the *Canvey Reports* and the *Rijnmond Report* and by Philipson (1980), Dale and Croce (1985), D.A. Jones (1985), Sellers, Luck and Pantony (1985), D.F. Cooper and Chapman (1987) and P. Roberts (1990).

The classification of initiating events and hazard scenarios for the refrigerated storage of liquefied gas shown in Table 22.2 is broadly applicable to LNG.

Considering some of the accounts mentioned, the treatment given by Kopecek (1977) is fairly general but includes a somewhat more detailed treatment than is generally found of the following natural events: (1) severe winds and tornadoes, (2) storm waves, tsunamis, (3) earthquakes and (4) meteorites.

R.A. Cox, Comer *et al.* (1980) deal with the hazard assessment of terminals rather than storage *per se*. The storage which they considered is a double integrity tank with inner steel and outer concrete walls and an earthen berm. They give for catastrophic failure of the inner tank leading to outer roof collapse and for partial fracture of the outer roof due to overpressure typical frequencies of 2×10^{-6} and 2×10^{-5}/year, respectively. They also give a typical failure frequency of 2×10^{-6}/year for catastrophic failure of a refrigerated ethane storage tank.

The accounts by Nassopoules (1982) and Closner and Wesson (1983) are concerned primarily with tank system designs, the former with a membrane system and the latter with double wall systems. Both give detailed consideration to the scenario of a tank fire in an adjacent tank. Closner and Wesson also consider a release from the inner tank, and earthquakes, missiles and blast.

D.A. Jones (1985) reviews refrigerated LNG storage systems, identifies five basic design concepts and summarizes the hazard assessments performed for installations embodying each of these concepts. Details of the assessments are sparse except for the Canvey studies. He does, however, give the following summary of the overall risks for exemplars of three of the five types of system:

Design	*Individual risk* (*fatality*) (year^{-1})	*Societal risk* ($\geq$10 *fatalities*) (year^{-1})
1. Single wall tank + low bund	2×10^{-6} 1.8×10^{-6}	9.3×10^{-6} 5.5×10^{-6}
2. Single wall tank + high bund	4×10^{-12} 8.5×10^{-9}	Negligible[a] 9×10^{-8}[b]
3. Double integrity tank system	Nil	Nil

[a] No more than two offsite casualties.
[b] Risk for 100–1000 casualties.

The overview of hazard assessment methodology by Napier and Roopchand (1986) quotes the frequency estimates for LNG terminals given by R.A. Cox, Comer *et al.* and those of release duration on LNG plants given by H.H. West, Pfenning and Brown (1980). Napier and Roopchand also give information on models for vaporization, heavy gas dispersion, pool fires, flash fires and VCEs.

The account by P. Roberts (1992) refers to a hazard assessment of a double integrity LNG tank with a prestressed concrete outer wall. Failure of the tank roof was considered and the consequences found to be limited, provided the integrity of the tank walls was maintained. An analysis was undertaken to demonstrate the integrity of the outer wall. Consideration was given to the various initiating events such as earthquakes, severe impacts, frost heave, settlement and blast. The risk was assessed as negligibly low.

Further principal sources of information on the frequency or probability of events, on the consequences and on the assessed risk for LNG storage are the *Canvey Reports* and the *Rijnmond Report*.

22.34 Ammonia Storage Hazard Assessment

Overviews of the hazard assessment of ammonia pressure and refrigerated storage are given in the *Canvey Reports* (HSE, 1978b, 1981a) and overviews of pressure storage are given in the *Rijnmond Report* and by Resplandy (1967). Guidance on safety cases for ammonia has been issued by the CIA (1989 GN1). Specific hazard assessments of ammonia pressure and refrigerated storage are given in the *Canvey Reports*, of pressure storage in the *Rijnmond Report* and of refrigerated storage by Squire (1991).

The classification of initiating events and hazard scenarios for the pressure and refrigerated storage of toxics shown in Table 22.2 is broadly applicable to ammonia.

The hazard assessments of ammonia storage in the first *Canvey Report* and the *Rijnmond Report* are described in Appendices 7 and 8, but mention may be made here of the scenarios considered in those studies.

For the Fisons ammonia pressure storage sphere the First *Canvey Report* considers for the vessel occurrences of spontaneous failure, engulfment in fire, blast effects, and missile impact. Ignition of the thermal insulation on the vessel was identified as a possible scenario, but was quickly discounted. The Shell refrigerated ammonia storage tank system was of the high bund type. For this tank the report considers the scenario of a fire engulfing the bund wall. Apart from this, the report states: 'The concrete collar ensures that the failure of the main tank cannot create a major hazard. The actual consequence of inner tank failure with the bund intact is virtually zero'. Various events initiating release from pipework associated with the storage were also taken into account. By the time of the Second *Canvey Report*,

both the pressure storage sphere and the refrigerated storage tank were no longer in use.

One of the six objects studied in the *Rijnmond Report* was the UKF ammonia pressure storage sphere. Initiating events considered were catastrophic failure of the vessel, a major crack in the vessel and full bore fracture of the liquid and vapour lines on the vessel.

An account is given by Squire (1991) of measures for enhancing the integrity of a refrigerated ammonia storage tank, which includes reference to a hazard assessment. The site handles a number of toxic substances, but the ammonia tank was assessed as constituting 50% of the total risk. Scenarios considered included catastrophic failure and rollover, or at least thermal overload, of the tank, and release from large pipework.

As indicated, the main sources of information on the frequency or probability of events, on the consequences and on the assessed risk for ammonia storage are the First *Canvey Report* and the *Rijnmond Report*.

22.35 Notation

Section 22.4

A surface area of pool (m^2)
C calorific value of liquid (kJ/kg)
D diameter of tank (m)
k_1 constant
Q heat radiated from the flame envelope (kW)
r liquid burning rate (m/s)
ρ density of liquid (kg/m^3)

Section 22.8

Equations 22.8.1 and 22.8.2
A total wetted surface (ft^2)
F environmental factor
Q total heat absorption (BTU/h)

Equations 22.8.3 and 22.8.4
C net calorific value of liquid in pool (kJ/kg)
h height of flame (m)
I intensity of heat radiation from the flame envelope (kW/m^2)
L length of pool (m)
Q heat emitted by fire (kW)
W width of pool (m)
ρ density of liquid (kg/m^3)

Section 22.10

T absolute temperature of liquid
x mole fraction of methane
α coefficient of expansion of liquid with respect to concentration
β coefficient of expansion of liquid with respect to temperature
ρ density of liquid

Section 22.11

Equation 22.11.1
R interface stability parameter
S concentration of impurity (mass fraction)
T absolute temperature of liquid
α coefficient of expansion with respect to temperature
β coefficient of expansion with respect to concentration

Equation 22.11.2
b boil-off rate
C_p specific heat of liquid
g acceleration due to gravity
H_v latent heat of vaporization of methane
k thermal conductivity of liquid
T_n absolute temperature of liquid in top or nth cell
T_s absolute saturation temperature of methane in LNG
μ viscosity of liquid
ρ density of liquid
ρ_o average reference density of liquid

Section 22.21

Subsection 22.21.4
h height of bund
H original height of liquid
L distance between tank wall and bund
R radius of tank
x, y dimensions of bund walls

Subsection 22.21.8
g acceleration due to gravity
h initial height of liquid in tank
M_f effective fluid mass
M_s effective mass of tank shell
R resistance to flow
t time
u velocity of fluid
x distance
ρ density of fluid

Section 22.24

Equation 22.24.1 only
η filling ratio
ρ_p density of liquid at reference temperature
ρ_w density of water at 15°C
ϕ fractional free space

Equation 22.24.2 only
g_i specific gravity of liquid at reference temperature
g_t specific gravity of liquid at its lowest likely temperature of filling
U_{max} maximum permissible volume
V internal volume of vessel

23 Transport

Contents

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So far the loss prevention problems discussed have been principally those of fixed installations. It is necessary, however, to consider also the transport of hazardous materials.

Some aspects of this transport which need to be considered include:

(1) regulatory control;
(2) classification;
(3) packaging and labelling;
(4) transport containers;
(5) hazards;
(6) hazard assessment;
(7) emergency planning.

For each mode of transport consideration has to be given to:

(1) controls and codes;
(2) hazard scenarios;
(3) design;
(4) operation.

In addition, the features particular to a mode must be considered.

A general account of regulatory controls and of codes applicable to transport internationally and in the UK has been given in Chapter 3. More detailed information on controls and codes is given in the following sections for road, rail, waterway, pipeline and sea transport.

A major source of information on transport and the associated hazards and risks is *Major Hazard Aspects of the Transport of Dangerous Substances* by the Advisory Committee on Dangerous Substances (ACDS, 1991) (the ACDS *Transport Hazard Report*). This report deals with marine, road and rail transport, and describes the regulatory regimes and transport environments as well as the hazards and risks. It considers in particular four substances which are both representative as well as themselves constituting a large proportion of the movements of dangerous substances: motor spirit, liquefied petroleum gas (LPG), ammonia and chlorine. The report also deals with explosives and ammonium nitrate. The ACDS *Transport Hazard Report* is described in more detail in Appendix 17.

Selected references on the transport of hazardous materials are given in Table 23.1.

23.1 General Considerations

The ability to transport the raw materials to and the products from the plant is very important in determining the viability of a project. This aspect was briefly considered in Chapter 1 in relation to ethylene plant economics.

The type of transport used may greatly affect the storage requirements. A mode of transport which involves larger but infrequent deliveries is, in general, likely to require more storage than one which gives continuous flow. Ship, rail, road and pipeline thus constitute a spectrum of modes of transport ranging from large discrete to continuous deliveries. The associated storage requirements have corresponding economic and safety implications.

In transport as in other aspects of loss prevention, training is of the greatest importance. It is essential that

Table 23.1 *Selected references on the transport of hazardous materials*

NRC (Appendix 28 *Transport*); D.R. Davis (1958); R. Lee (1961); Anon. (1962a); J.E. Browning (1969b); Pence (1969); Byrd (1970); J.R. Hughes (1970); McConnaughey *et al.* (1970); A.W. Clarke (1971a,b); A.B. Kelly (1971); NTSB (1971); Bigelow (1972); Institution of Fire Engineers (1972); *Chemical Engineering* (1973a); NFPA (1973/10); Pignataro (1973); Walmsley (1973, 1974); W.S. Wood (1973, 1982b); MCA (1974 TC-20); Unwin, Robins and Page (1974); Westbrook (1974); Gay (1975); Malcolm (1975); Meadowcroft (1975); Peeler (1975); Whitbread (1975); Cantilli *et al.* (1976); D.R. Davies and Mackay (1976); Horodniceanu *et al.* (1976, 1977); Philipson (1976); Appleyard (1977); CONCAWE (1977 7/77); Druijff (1977); Flynn and Morrissette (1977); John (1977); Mullins (1977); Zedde (1977); ICE (1978); Horodniceanu and Cantilli (1979); IBC (1979/4, 1981/20, 1982/37, 1985/65, 1992/94, 1993/106); Napier (1979a); Nimptsch (1979); Luckritz and Schneider (1980); Cannon (1983b); Vumbaco (1983); Bierlein (1984); Ichniowski (1984, 1987); Belardo, Pipkin and Seagle (1985); Ackermann (1986); Carnes (1986); Kazarians, Boykin and Kaplan (1986); Kletz (1986j); Dryden and Gaweckie (1987); Frey and Handman (1987); Walker (1987); CIA (1989 RC27); Belanger (1990); Burns (1990); N. Lees (1990); Beroggi and Wallace (1991); Canadine (1991); UN (1991); Croner Publishing (1993); B. Davies (1993)

Containers, packaging
Dowling (1960); Norden (1960d); Ayers and Rhodes (1963); Uncles (1966); Home Office (1968); McKinley (1968); J.E. Browning (1969b); A.W. Clarke (1971b); Lunn (1971, 1975); Raymus (1973); Swinbank (1973, 1975); Bohlman (1975); DoE (1975/5); G.J. Lewis (1975); R.K. Roberts (1975); Steel (1975a,b); Department of Trade (1977); IMCO (1977); H. Morris (1977); Bond (1978); Boocock (1978); Cronin (1978); Gregory (1978); Anon. (1980 LPB 32, p. 15); Chlorine Institute (1980 Publ. 17, 1985 Publ. 8); Petherbridge and Kinder (1983); HSE (1986 CS 17, HS(G) 26, 1992 CRR 37, HS(G) 78); Schilperoord (1986); Ashmore (1988 LPB 80); Blümel and Schulz-Forberg (1989); Shattes (1986); Anon (1990c); NFPA (1990 NFPA 386); CIA (1991 RC35, RC37, 1992 RC59); UN (1991); Simpson and Jones (1992)

Gas cylinders
BCGA (Appendix 27, 1988 GN2); CGA (Appendix 28, 1966/1); HSE (1990 IND(G) 78(L))

Labelling
MCA (SG-18, 1976/24); D.L. Davies (1975); Rees (1975); Anon. (1978j); Williamson (1978); Anon. (1979h); Selikoff (1979); Anon. (1980 LPB 32, p. 15); O'Connor and Lirtzmann (1984)

Radio-telephones
ACDS (1991); British Gas (1992 GBE/DAT31); IP (1993 TP 20)

COSHH in transport
CIA (1991 RC50)

Road
DoE (n.d., 1974, 1976a); DoT (n.d., 1978, 1987a,b, 1992b, 1993a,b); NSC (n.d./5, 8); NTSB (Appendix 28 *Highway Accident Reports*); OIA (Publ. 711); Brantley (1964); Steymann (1966); BCISC (1967/6); Danskin (1969); Olsen (1969); H. Lewis (1971); Rohleder (1971); Brobst (1972); Harvison (1972, 1973, 1981); Ramsey (1972); CIA (1973/4, 5, 1988 CE4, PA16, 1990 RC26); DoE (1974/5); IMechE (1975/20, 23, 1976/26, 30, 1977/32, 1978/48, 1983/72); Rutherford (1975); P.N. Anderson (1977); Ashton (1977); Davison (1977); Hudson (1977); Rickett (1977); Watters (1977); Anon. (1978 LPB 19, p. 1); HSE (1978b, 1981a, 1983 GS 269 1990 IND(G) 96(L)); Napier (1979a); Anon. (1981 LPB 39, p. 17); Botkin (1981); Chlorine Institute (1981 Publ. 76, 1984 Publ. 49); Eiber (1981); Heller (1981); A.D. McLean (1981); Rudram and Lambourn (1981); ASME (1982/191); Anon (1984jj,ll); M. Griffiths and Linklater (1984); Jäger (1984); Sewell (1984a); Bressin (1985); Hawkins (1985); Lambourn (1985); Allsop *et al.* (1986); API (1986 Publ. 2219, 1988 RP 1004); I.A. James (1986); Kessler (1986); Anon. (1987 LPB 76, p. 30); Grime (1987); Walker (1987); Glickman (1988); Canadine and Purdy (1989); Harwood, Russell and Viner (1989); Saccomanno *et al.* (1989); Anon. (1990c); Anon. (1990 LPB 94, p. 10); Gorys (1990); Harwood, Viner and Russell (1990); NFPA (1990 NFPA 385, 512, 513, 1992 NFPA 498); Ouellette, Hoa and Li (1990); Rhyne (1990); Saccomanno, Shortreed and Mehta (1990); Steward and van Aerde (1990a,b); ACDS (1991); UN (1991); Croner Publishing (1993); DTp (1993a); Purdy (1993); IP (1994/4, 5)
Pressure relief: Hawksley (1990 LPB 91); UN (1991)

Rail
BR (n.d.a,b); NTSB (Appendix 28 *Railroad Accident Reports*); Danielson (1964); Walton (1964); Heller (1965); Steymann (1966); Engel (1969); ASME (1971/188); Barron (1971); Maughan (1971); E.A. Phillips (1971); AAR (1972); Banks (1972); O'Driscoll (1972, 1975b, 1976, 1978); Stanek (1973); MCA (1974 TC-7); CIA (1975 PAl); Fizer (1976); P.J. Lynch (1977); HSE (1978b); Chlorine Institute (1979 Publ. 66); Napier (1979a); National Supply Co. (UK) Ltd (1979); R.K. Cooper (1980); Taig (1980); Sanderson (1981); IMechE (1983/72); Schlitchtärle and Huberich (1983); Ichniowski (1984); Jopson and Bale (1984); Hawkins (1985); Glickman (1988); J.L. Woodward and Silvestro (1988); Canadine and Purdy (1989); G.O. Rogers and Sorenson (1989); Saccomanno and El-Hage (1989); Saccomanno *et al.* (1989); J.L. Woodward (1989b); Gorys (1990); Rhyne (1990); Saccomanno, Shortreed and Mehta (1990); ACDS (1991); DTp (1993b); Janes Information Group (1993c); Tenniswood, Sharp and Clark (1993)

Tunnels
W.E. Baker *et al.* (1979); Larson, Reese and Wilmot (1983); Anon. (1985ee); HSE (1985e); A. Jones (1985); Considine (1986); M.M. Grant (1989); NFPA (1992 NFPA 502); Charters, Gray and McIntosh (1994)

Waterways
Martinson (1964); H.P. Nelson (1964); Steymann (1966); Briley (1967); Sohnke (1971); French and Richards (1973); Backhaus and Janessen (1974); Chlorine Institute (1984 Publ. 79); Ligthart (1980); Backhaus (1982); Boniface (1989); J.R. Thompson *et al.* (1990); API (1991 RP 1125)

Pipelines
AGA (Appendix 28); ASCE (Appendix 28, 1965/19 1975/5, 1978/7, 1979/8, 1983/14, 1984/17, 20, 1988/37, 1991/44); ASME (Appendix 28 *Pipeline Engineering*); British Gas (Appendix 27, 28); NTSB (Appendix 28 *Pipeline Accidents Reports*, 1978); Henderson (1941); Anon. (1964c); Lennart (1964); H.P. Nelson (1964); IGasE (1965/7, 1967/89, 1976/10); F.C. Price (1965, 1974a,b); BRE (1966/3); Chilton (1966); FPC (1966); Hubbard (1967); IP (1967 Model Code Pt 6); N.W.B. Clarke (1968); Inkofer (1969); Rohleder (1969); Prescott (1970); Wasp, Thompson and Snoek (1971); Cleveland and Young (1972); Davenport and Brameller (1972); Walker, Coulter and Norrie (1972); Weiner, Mercer and Gibson (1972); Gibson, Knowles and Mercer (1973); N.W. Roberts and Stewart (1973); Smelt and James (1973); Devine *et al.* (1974); DOT (1974); C.C. Hale (1974); Anon. (1975f); L.J. Allen (1975); DOT, OPS (1975); Luddeke (1975); Newmark and Hall (1975); Szilas (1975); CONCAWE (1977 9/77); Demars *et al.* (1977); DOT, OPSO (1977b); Gulf Publishing Co. (1977); IGasE (1977 Comm. 1044, IGE/TD 1); Knowles, Tweedle and van der Post (1977); McKay *et al.* (1977); Sterling (1977); Dickson (1978); HSE (1978b,d, 1980a,c); ASME (1979 *Pressure Piping Code* B31.4, 1989 *Pressure Piping Code* B31.8); Bryce and Turner (1979); Muleski, Ariman and Auman (1979); Riley (1979); Shinozuka, Takadu and Ishakawa (1979); Tasucher and Streiff (1979); Wang and Cheng (1979); Thorley (1980); M.J. Turner (1980); DoI (1981); de la Mare and Andersen (1981); Sheffy (1981); Stephenson (1981a); Chlorine Institute (1982 Publ. 60); N.C. Harris (1982); Sabnis, Simmons and Teuscher (1982); Whalley and Long (1982); Whittaker *et al.* (1982); Considine (1983); Diab (1983); API (1984/14, 1985 Publ. 1108, 1988 Std 1104, 1991 RP 1107, 1110, 1118, 1119, 1120, 1993 RP 1102, 1109, 1113); Blything (1984 SRD R326); Forsyth (1984); G.G. King (1984); Pipeline Industries Guild (1984); Berryman and Daniels (1985); Bruce (1985); Fearnehough (1985); Jinsi (1985); Kipin (1985); Lund *et al.* (1985); Stripling, Khan and Dillon (1985); True (1985); Darton (1986); Redman (1986a,b); BP Petroleum Development Ltd (1988); C.C. Hale and Lichtenberg (1988); NRC, Transportation Research Board (1988); Bolt and Logtenberg (1989); D.A. Carter (1991); Colombari *et al.* (1992); Ahammed and Melchers (1993); DTI (1993); de la Mare and Bakouros (1994)
Corrosion protection, cathodic protection: AGA (1979/29, 1990/67); British Gas (1992 GBE/ECP)
Plastic pipelines: British Gas (1985 Comm. 1281, 1986 BGC/PS/PL2); AGA (1989/12)
Trenchless technology: International Society for Trenchless Technology (1991); ACGIH (1992/86)

Sea
ICS (Appendix 27, 1974); IP (n.d.); NTSB (Appendix 28 *Marine Accident Reports*); OCIMF (Appendix 27); SIGTTO (Appendix 28); Wardle (n.d.); Minorsky (1959); Burgoyne (1965a); Rawson and Tupper (1968–); Comstock and Robertson (1969); Dickinson (1969); Dyer (1969); Advisory Committee on Carriage of Dangerous Goods by Sea (1971); DTI (1971); Lakey (1971, 1973,

1976); Neal (1971); Page and Gardner (1971); Stirling (1972); H.D. Williams (1972, 1973); F.A. Smith (1973); European Petroleum Organisations (1974); Kahn, Talbot and Woodward (1974); Mostert (1974); Boe and Foleide (1975); Chapman (1975); Eisenberg, Lynch and Breeding (1975); Swinbank (1975); Henderson, Srinivansan and Gower (1976); NPC (1976); J.J. Smith (1976); Davison (1977); IMCO (1977); Mullins (1977); Tanker Safety Group (1977); HSE (1978b, 1981a); ICS/OCIMF (1978); van Poelgeest (1978); Snow (1978); Planning Research Corp. (1979); Böckenhauer (1980); Rutherford (1980); B. White (1980); Gardenier (1981); Gregory (1981); Aldwinkle and Slater (1983); van den Brink (1983); Georgas (1983); Hendrickx and Lannoy (1983); van der Horst and van der Schaaf (1983); Hough (1983); Preston (1983); Colonna (1984, 1986); Fleming (1984); Champness and Jenkins (1985); ACDS (1991); API (1991 RP 1140, 1993 RP 1139); DoT (1992); Janes Information Group (1993b); Paris Memorandum (1993); Donaldson (1994); Gilbert (1994); Hodges (1994); K. James (1994); Jenkins (1994); Rawson (1994)

Codes, classification rules, regulation: A.W. Clarke (1971a); DTI (1971); Lakey (1971, 1973, 1976); Kvamsdal (1973); R.K. Roberts (1973); International Chamber of Shipping (1974); IMCO (1977); Anon (1984r); R. Pearson (1984); J. Smith (1994)

Cargo compatibility: Flynn and Rossow (1970a,b); Flynn and Morrisette (1977); Morrisette (1979)

Hazard information systems: DOT, CG (1974a–d); Butt (1975); Myatt (1975); Rappaport (1975); Willis and Cece (1975)

Human factors: Page (1971); Leeper (1973); Hooft, Keith and Porricelli (1975); D. Anderson, Istance and Spencer (1977)

Vessel design: Comstock (1967); Rawson and Tupper (1968–); Barnaby (1969); J. Cox (1971); R.K. Roberts (1973, 1983); Hansen and Vedeler (1974); Chapman (1975); N. Jones (1976, 1983); Eyres (1978); HSE (1978b, 1981a); Kitamura, Okumoto and Shibue (1978); Böckenhauer (1982, 1985); Clayton and Bishop (1982); Farrell (1982); Huther and Benoit (1983); Jean and Lootvoet (1983); Kinkead (1983, 1985 SRD R324); Betille and Lebreton (1986); Egge and Böckenhauer (1991)

Cargo tanks: Schampel and Steen (1975, 1976); Böckenhauer (1982)

Ship movement: A.G. Robinson (1971); Bovet (1973); Computer Sciences Corp. (1973); P.W.W. Graham (1973); US Coast Guard (1973); McDuff (1974); Eda (1976); J.W. Miller, Schneider and Varchok (1976); NPC (1976); Port of London Authority (1977); HSE (1978b, 1981a); Transportation Systems Centre (1978); ASCE (1980/11, 1983/14, 1986/28, 1989/37); Ligthart (1980); Brok and van der Vet (1984); Mankabady (1982); Technica (1985); ACDS (1991)

Collision, grounding: E. Chen (1975); Kinkead (1978 SRD R91, 1985 SRD R342); Vaughan (1978); Ligthart (1980); Poudret *et al.* (1981); Asadi and Vaughan (1990): ACDS (1991)

Ship–shore transfer: B. White (1980); Armitage (1983); T.B. Morrow *et al.* (1983); Bond (1986 LPB 71); Holtkamp and Keech (1989)

Emergency response, planning: Preston (1983); NFPA (1990 NFPA 1405); ACDS (1991)

Pollution: Stubberud (1973); European Petroleum Organisation (1974); Hann and Jensen (1975); Lakey (1976); Fleming (1984)

Tank purging, cleaning, inerting and flame protection: Page and Gardner (1971); Bang and Birkeland (1973); Boddaert (1975); Harth (1975); Savage (1975); Schampel and Steen (1975, 1976, 1977); Steensland, Askheim and Vossgard (1975); R.P. Wilson and Atallah (1975); Berkel (1982); Astleford, Morrow and Buckingham (1983); Anon. (1984s); Astleford, Bass and Colonna (1985)

Vapour emission, vapour emission control: T.B. Morrow (1980, 1982b, 1985); T.B. Morrow *et al.* (1980); API (1989/17, 1991 RP 1124, 1992/20); Lawrence and Cross (1994)

Fire, explosion: Burgoyne (1965a); Schön (1968); Page and Gardner (1971); Victory and Roberts (1971); Wilse (1974); Barreto (1975); Goland and Critelli (1975); Kitagawa (1975); J.H. Lee, Knystautas *et al.* (1975); Rushbrook (1979); Takeda (1988)

Static electricity: H.R. Edwards (1983); J.S. Mills and Oldham (1983); M.R.O. Jones and Bond (1984, 1985)

Fire protection: Page and Gardner (1971); Tanner (1976); Rushbrook (1979); Anon. (1980o, 1982k); Dicker and Ramsey (1983); Dimmer (1986); Wynne (1986); Gebhardt (1989); McKenna (1989); ACDS (1991); NFPA (1993 NFPA 306)

Containers, packing: Savi (1971); Stubberud (1971); Buschman (1973); Kemler (1975); Swinbank (1975); Department of Trade (1977); UN (1991)

Ports, port storage

McKinley (1968); Meijer (1968); Dickinson (1969); Murdoch (1971); Siccama (1971); Bohlin (1973); J.R. Bradley (1973); Vossenaar (1975); Davison (1977); Hartlich (1977); HSE (1978b, 1980 HS(G) 7, 1981a, 1986 GS 40); ASCE (1980/11, 1983/15, 1986/29, 1989/38); Bryce (1980); Gebhardt (1980, 1989); P. Lewis (1981); NFPA (1990 NFPA 307); ACDS (1991)

Air

Pike (1975a,b); CAA (1977); K. Warner (1981); Wilkinson (1989); Janes Information Group (1993a)

Particular chemicals

Ammonia: Heller (1965, 1981); Briley (1967); Inkofer (1969); Olsen (1969); Rohleder (1969, 1971); Medard (1970); Cato and Dobbs (1971); Caserta (1972a); C.C. Hale (1974); CIA (1975/9, PAI); Eisenberg, Lynch and Breeding (1975); Luddeke (1975); O'Driscoll (1975a); Sterling (1977); Eiber (1981); DCMR (1985); Josefson (1987); C.C. Hale and Lichtenberg (1988)

Chlorine: Chlorine Institute (Appendix 28, 1979 Pmphlt 66, 1981 Pmphlt 76, 1982 Pmphlt 60, 1984 Pmphlt 49, 79, 1986 Pmphlt. 1); Danielson (1964); H.P. Nelson (1964); R.L. Mitchell (1971, 1972, 1982); Mathiesen, Bakke and Boe (1973); Westbrook (1974); Eisenberg, Lynch and Breeding (1975); Macdonald (1977); DCMR (1985); Hunter (1988); J.L. Woodward and Silvestro (1988); Canadine and Purdy (1989); Rhyne (1990)

Explosives: P.A. Davies (1990, 1993); ACDS (1991); Sorenson, Carnes and Rogers (1992); Gilbert, Lees and Scilly (1994a–i)

LNG (*see* Table 11.23)

LPG: Faridany and Ffooks (1983); Jäger (1984); Puklavec and Lindenau (1985); Davenport (1988); Anon. (1990c)
Monomers: Butcher and Sharpe (1983); Kurland and Bryant (1987)
Petroleum: J.R. Hughes (1970); Page and Gardner (1971); F.A. Smith (1973); IP (1982 MCSP Pt 6)

Particular chemicals: other chemicals
Carbon dioxide: Brumshagen (1983)
Ethylene: Anon. (1962f); Waddams and Cann (1974); McKay *et al.* (1977); Backhaus and Ölschlager (1985)
Lead additive: Associated Octel (1972 Bklt 23/72, 1975 Bklt 22/75)
Liquefied gases: Purdy *et al.* (1988)
Peroxides: Anon. (1984ee)
Polybrominated biphenyls (PBBs): Jacobs, Chou and Tiedje (1976); Kay (1977)
Radioactive materials: Pike (1975a,b); DoE (1975/5); Wilson (1981 LPB 42); Tuler, Kasperson and Ratick (1989)
Self-heating materials: Stone, Williams and Hazlett (1976)
Sulphur: Landry and Hiller (1975)
Vinyl chloride: Dowell (1971); Kogler (1971); O'Mara, Crider and Daniel (1971); Wheeler and Sutherland (1975); Mukerji (1977)

Fire (*see* Tables 16.1 and 16.2)
Spill control (*see also* Table A11.1)
R.L. Mitchell (1971, 1972, 1982); Baier *et al.* (1975); Brugger and Wilder (1975a,b); G.W. Dawson (1975); Pilie *et al.* (1975); Bulloff and Sinclair (1976); Froebe (1976, 1985); Temple *et al.* (1978); Thorne (1978a); Zadic and Himmelman (1978); R.E. Warren (1978); Tenzer *et al.* (1979); R.H. Hall *et al.* (1980); Norman and Dowell (1980); Temple *et al.* (1980); Anon. (1982h); Cumberland (1982); R.M. Hiltz (1982); R.L. Mitchell (1982); Scholz (1982); H.M. Freeman (1984); Neely and Lutz (1985); P.J. Warren (1985); Deckert (1986)
Leak control, sealing: Anon. (1977j); R.L. Mitchell (1982)

Hazard assessment
Buschmann (1968); Crouch (1968); D.L. Katz (1968); Lindeijer (1968); McConnaughey (1971); Siccama (1971); McQueen *et.al.* (1972); Coates (1973); Fortson *et al.* (1973); French and Richards (1973); Kneebone and Boyle (1973); McKinley (1973); Swalm (1973); Woodward-Lundgren and Associates (1973); Dunn (1974); Dunn and Tullier (1974); A.D. Little (1974); Philipson (1974b); Allan, Brown and Athens (1975); BDM Corp. (1975); Bohlman (1975); Domalski and Tsang (1975); Droppo and Watson (1975); Fedor, Parsons and de Coutinho (1975); Gardenier *et al.* (1975); Humphrey (1975); Philipson and Schaeffer (1975); Simmons (1975); Simmons and Erdmann (1975); Tihansky (1975); Frenkel and Hathaway (1976); USCG (1976a); Stoehr *et al.* (1977); Tanker Safety Group (1977); HSE (1978b,d, 1980c, 1981a); Napier (1979a); Jennsen and Larsen (1980): N.C. Harris (1982); Philipson and Napadensky (1982); Bello, Romano and Dosi (1983); Bergmann and Riegel (1983); van der Horst and van der Schraaf (1983); Lucas, Roe and Waterlow (1983); Windebank (1983); DCMR (1985); N.C. Harris and Roodbol (1985); Moffow (1985); Ackermann (1986); Allsop *et al.* (1986); D.A. Jones and Fearnehough (1986); Medland (1986); Purdy *et al.* (1987, 1988); van Aerde, Stewart and Saccomanno (1988); Cummings and Bradley (1988); Ormsby and Le (1988); J.L Woodward and Silvestro (1988); Abkowitz and Cheng (1989); Andreassen and Gjerstadt (1989); Canadine and Purdy (1989); Guy (1989); Hoftijzer, van der Schaaf and Lupker (1989); Hubert and Pages (1989); V.C. Marshall (1989a, 1991b); Sellers and Bendig (1989, 1990); Birk, Anderson and Coppens (1990); Ramachandran (1990b); Saccomano, Shortreed and Mehta (1990); J.R. Thompson *et al.* (1990); ACDS (1991); Brockhoff (1992); R.T. Hill (1992); Goh, Tan and Ching (1993); Medhekar, Gekler and Bley (1993); Purdy (1993); Romer *et al.* (1993); Song, Black and Dunn (1993); Tenniswood, Sharp and Clark (1993)
Comparative studies—modes of transport: Westbrook (1974); Beattie (1989); Saccamano *et al.* (1989); ACDS (1991)
Comparative studies—alternative routes: Rhyne (1990); ACDS (1991),
Comparative studies—transport vs fixed installations: Haastrup and Brockhoff (1990); Haastrup and Styhr Petersen (1992)
Explosives: Chapman and Holden (1987 SRD R412); P.A. Davies (1990); ACDS (1991)

Transport statistics, transport accident statistics
Hicks *et al.* (1973); Gay (1975); DoE (1976b); Ichniowski (1987); ACDS (1991)
Road: North (1974); DoT (1982, 1985); CSO (1986); A. James (1986); Grime (1987); ACDS (1991); P.A. Davies and Lees (1991b, 1992)
Rail: ACDS (1991); P.A. Davies and Lees (1991a)
Rotorcraft: NTSB (1981)

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all personnel involved in the transport of chemicals are thoroughly trained in the properties of the chemicals and the associated hazards and in the normal operating and emergency procedures.

23.1.1 Modes of transport

The following modes of transport are used for the movement of hazardous materials:

(1) road;
(2) rail;
(3) waterway;
(4) pipeline;
(5) sea;
(6) air.

23.1.2 Transport movements

For the UK, information on the movements of hazardous materials is given in *Transport Statistics Great Britain 1991* by the Department of Transport (DTp, 1992b), which is part of an annual series.

Further data on the movements of hazardous materials by road and rail in the UK are quoted in the ACDS *Transport Report* and are given below in Sections 23.6 and 23.8, respectively.

For the USA, corresponding information is provided in the annual reports of the National Transportation Safety Board (NTSB). The NTSB *Annual Report* for 1979 states that there were in that year some 250 000 hazardous materials shipments per day. Reports of accidental releases numbered about 16 000 and there were 19 fatalities and 942 injuries. The breakdown of fatalities by commodity was as follows: gasoline 32.5%, liquefied petroleum gas 21.7%, chlorine 9.6%, corrosive liquids 9.6%, anhydrous ammonia 6%, aviation fuel 2.4%, compressed gas, 2.4% and others 15.6%. The *Annual Report* for 1991 quotes the same number of daily shipments of hazardous materials.

23.1.3 Transport conditions

The main sets of conditions for gas or liquid transport are:

(1) liquid at atmospheric pressure and temperature (atmospheric transport);
(2) liquefied gas under pressure and at atmospheric temperature (pressure transport);
(3) liquefied gas at atmospheric pressure and at low temperature (fully refrigerated transport);
(4) gas under pressure.

The behaviour of fluids released from such conditions has been described in Chapters 15 and 22. An account related specifically to transport is given by V.C. Marshall (1991b).

23.1.4 Transport hazards

The transport of hazardous materials may present a hazard to (1) the transporter, (2) the crew or (3) the public. The relative importance of these varies between the different modes of transport.

The hazards presented by the transport of chemicals are:

(1) fire;
(2) explosion;
(3) toxic release –
  (a) conventional toxic substances;
  (b) ultratoxic substances.

As with fixed installations, so with transport the most serious hazards arise from loss of containment.

Modes of transport such as road, rail, waterway and pipeline can give rise to release of flammable gas or vapour, which may result in a flash fire or a vapour cloud explosion, or of flammable liquid which may lead to a pool fire. Flammable liquid can also spread and then ignite, giving rise to a flowing fire. Jet flames may occur on the containers. The contained material may undergo a BLEVE or other form of explosion. In general, a flammable fluid is more likely to give rise to fire than to explosion.

An explosion hazard also exists with substances that are to some degree unstable.

If the material is toxic, release may result in a toxic gas cloud. Toxic or corrosive materials may also spread as liquids.

With waterway and sea transport, the release of vaporizable materials onto the water is liable to give rise to very rapid vaporization, resulting in a large vapour cloud.

Transport accidents are particularly liable to cause pollution, since material spilled is often not recovered, but is dispersed into the environment.

The initiating factor in a transport accident may be (1) the cargo, (2) the transporter or (3) the operations.

The cargo may catch fire, explode or corrode the tank; the transporter may be involved in a crash or derailment or fire; the operations such as charging and discharging may be wrongly executed.

Thus the events which can give rise to hazards include particularly (1) container failure, (2) accident impact, and (3) loading and unloading operations.

Although the attention in transport of hazardous materials by moving vehicles focuses on the injury caused by release from containment, fatalities also occur due to the movement of the vehicles themselves. This should be taken into account also, particularly in comparative studies of different modes of transport, since although the deaths from this cause in any one accident tend to be small in number, they may in total equal or exceed those from the releases.

23.1.5 Size of units

As with fixed installations, so with transport the question arises as to whether it is safer to handle a given quantity of hazardous material in a few large units or in many smaller ones. In particular, there is a wide range of possibilities with sea transport. The choice made affects not only the size of the ship but also that of the associated storage on land. In general, a small number of large units appears safer in the sense that the product of scale and frequency tends to be less. This is because with fewer units it is easier to achieve a more uniformly high standard of design and operation, and the frequency of incidents is less. The scale of the most serious accident, however, is greater. The problem has been considered by the Tanker Safety Group (1977), which has reviewed the historical experience with large crude oil tankers and supertankers.

23.1.6 Multi-use containers

The use of the same container to carry different chemicals is quite normal; it is fairly common practice in road tankers, barges, ships and pipelines. This not only creates potential problems of compatibility between materials carried, but also means that the carrier is less familiar with the substances he is transporting.

23.1.7 Loading and unloading

Many of the hazards associated with transport arise during loading or unloading. This aspect was treated in relation to storage in Chapter 22 and is considered only occasionally in this chapter.

23.2 International Codes

The transport of chemicals is an international activity and international codes assume a dominant role. These codes govern not only the classification, packaging and labelling of substances, but also the transport containers. There are four main codes which are relevant here and these are now described.

23.2.1 UN Transport Code

A basic code for international transport is provided by the *Recommendations on the Transport of Dangerous Goods* (United Nations, 1993) (the UN *Transport Code*).

Topics dealt with in the code include: (1) classification, including testing; (2) packing; (3) labelling; (4) transport containers, including intermediate bulk containers and tank containers; and (5) consignment procedures.

The classification of dangerous goods for transport given in the UN *Transport Code* provides a framework which is followed by other codes. The classification scheme, which is based on classification by class of substance, is shown in Table 23.2.

In addition to this classification, there is for Class 1, explosives, a further categorization by compatibility group. The compatibility groups are A–H, J–L, N and S. The general nature of these compatibility groups is illustrated by the following entries:

Group A Primary explosive substance.
Group B Article containing a primary explosive substance and not containing two or more effective protective features.

Dangerous goods of all classes other than Class 1, 2, 5.2, 6.2 and 7 are assigned for packing purposes to one of three groups according to the degree of danger which they represent:

Packing group
I Great danger.
II Medium danger.
III Minor danger.

The *Code* contains a set of specimen hazard warning signs for the labelling of dangerous goods. A selection of these is shown in Plate 21. Further details of the classification, packaging and labelling provisions of the code are given in Section 23.3.

The *Code* gives recommendations for the mechanical design, service equipment and pressure relief arrangements for transport containers, as described in Section 23.4. It also contains recommendations on consignment procedures, including packages and the provision of transport documentation. In addition to the general recommendations of the *Code*, there are special recommendations applicable to each class of substance.

Table 23.2 *UN* Transport Code*: classification of substances (United Nations, 1993)*

Class 1	Explosives
Division 1.1	Substances and articles which have a mass explosion hazard
Division 1.2	Substances and articles which have a projection hazard but not a mass explosion hazard
Division 1.3	Substances and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both but not a mass explosion hazard
Division 1.4	Substances and articles which present no significant hazard
Division 1.5	Very insensitive substances which have a mass explosion hazard
Division 1.6	Extremely insensitive articles which do not have a mass explosion hazard
Class 2	Gases
Division 2.1	Flammable gases
Division 2.2	Non-flammable, non-toxic gases
Division 2.3	Toxic gases
Class 3	Flammable liquids
Class 4	Flammable solids; substances liable to spontaneous combustion; substances which in contact with water emit flammable gases
Division 4.1	Flammable solids
Division 4.2	Substances liable to spontaneous combustion
Division 4.3	Substances which in contact with water emit flammable gases
Class 5	Oxidizing substances; organic peroxides
Division 5.1	Oxidizing substances
Division 5.2	Organic peroxides
Class 6	Poisonous (toxic) and infectious substances
Division 6.1	Poisonous (toxic) substances
Division 6.2	Infectious substances
Class 7	Radioactive materials
Class 8	Corrosive substances
Class 9	Miscellaneous dangerous substances

23.2.2 European Road Carriage Agreement (ADR)

The European code for international transport is the *European Agreement Concerning the International Carriage of Dangerous Goods by Road* (ADR) issued by the Department of Transport (DTp, 1993a).

The document contains the Articles of the Agreement and two Annexes, Annex A and Annex B. Annex A, Provisions Concerning Dangerous Substances and Articles, has three parts: Part I on general provisions, Part II on special provisions for substances in the various Classes, and Part III a set of appendices. These appendices cover the following topics: A1, stability and safety conditions relating to explosive substances and articles, flammable solids and organic peroxides; A2, containers for Class 2 substances, including aluminium alloy containers and containers for fully refrigerated gases; A3, tests for substances; A5, general packing conditions; A6, intermediate bulk containers; A7, Class 7, radioactive materials; A9, symbols and labels. A4 and A8 are not used.

Annex B, Provisions Concerning Transport Equipment and Transport Operations, has two parts and a set of appendices, Part I dealing with general provisions and Part II with special provisions for the various Classes whilst the appendices cover the following topics: B1, containers including fixed and demountable tanks, tank containers and reinforced plastic tanks; B2, electrical equipment; B3 certificates of approval for vehicles; B5 list of substances; and B6, certificate of driver's training. B4 is not used.

The provisions for classification, packaging and labelling provisions are considered further in Section 23.3 and those for transport containers are discussed in Section 23.4.

23.2.3 International Rail Carriage Regulations (RID)

There have for some time been a set of Uniform Rules concerning the Contract for International Carriage of Goods by Rail (CIM) and there is a Convention concerning International Carriage by Rail (COTIF) of 1980. The international code for rail transport is the *Regulations Concerning the International Carriage of Dangerous Goods by Rail* (RID) issued by the Department of Transport (DTp, 1993b); it constitutes Annex 1 of the Uniform Rules.

The document, which is itself an annex, contains extracts from the Articles of the Convention and from the Uniform Rules, which are Appendix B of the Convention. It has three parts: Part I on general regulations, Part II on special regulations for substances in the various Classes, and Part III a set of appendices. These appendices cover the following topics: I, stability and safety conditions relating to explosive substances and articles, flammable solids and organic peroxides; II, containers for Class 2 substances, including aluminium alloy containers and containers for fully refrigerated gases; III, tests for substances; V, general packing requirements; VI, intermediate bulk containers; VII, Class 7, radioactive materials; IX, symbols and labels; X, construction, testing and use of tank containers; and XI, construction, testing and use of tank wagons. IV is not used.

The provisions for classification, packaging and labelling provisions are considered further in Section 23.3 and those for transport containers are discussed in Section 23.5.

23.2.4 *International Maritime Dangerous Goods (IMDG) Code*

For sea transport the relevant code is the *International Maritime Dangerous Goods Code* (*IMDG Code*) issued by the International Maritime Organization (IMO, 1990 IMO-200). The classification for dangerous goods for maritime transport given in the *IMDG Code* is again virtually the same as that of ADR, as shown in Table 23.2.

23.3 Classification, Packaging and Labelling

There is a large international trade in dangerous goods and it is particularly important that the arrangements for the classification, packaging and labelling of these substances be accepted internationally.

23.3.1 Regulatory controls and codes

As already described, the international codes governing the transport of dangerous goods, namely the UN *Transport Code*, ADR, RID and the *IMDG Code*, give detailed recommendations on classification, packaging and labelling.

Classification, packaging and labelling is the subject of EC Directive 67/548 (the Dangerous Substances Directive). In the UK this directive was implemented for the road transport of hazardous materials by the Classification, Packaging and Labelling Regulations (CPL) 1984. The associated Approved Codes of Practice (ACOPs) are COP 19 *Classification and Labelling of Substances Dangerous for Supply and/or for Conveyance by Road 1984*, Revision 1 (HSE, 1990) and COP 40 *Packaging of Dangerous Substances for Conveyance by Road 1984*, Revision 2 (HSE, 1990). Guidance is given in HS(R) 22 *A Guide to the Classification, Packaging and Labelling Regulations 1984* (HSE, 1985). Also relevant is COP 33 *Transport of Compressed Gases in Tube Trailers and Tube Containers* (HSE, 1989).

The Chemicals (Hazard Information and Packaging) Regulations 1993 (CHIP) now supersede the CPL Regulations. In consequence, the ACOPs and guidance for the latter become out of date, but at the time of writing replacements have not been issued.

These regulations are complemented by the Road Traffic (Carriage of Dangerous Substances in Packages etc.) Regulations 1992 and the Road Traffic (Carriage of Dangerous Substances in Road Tankers and Tank Containers) Regulations 1992, which are described in Section 23.5.

Guidance on cargo transport units (CTUs) for marine transport is given in HS(G) 78 *Container Packing* (HSE, 1992).

For explosives there are the Classification and Labelling of Explosives Regulations 1983 (CLER) and the Packaging of Explosives for Carriage Regulations 1991.

23.3.2 UN Transport Code

The classification scheme of the UN *Transport Code* has been given in outline in Table 23.2. The *Code* gives guidance on assignment to a class, or a division within a class. For some classes of substances, notably explosives and organic peroxides, there are specified tests. These tests, and the flow charts for assignment, are described in Chapter 8.

For Class 3, Flammable liquids, there is a hazard grouping based on boiling point and flashpoint. This is

Packing group	*Flashpoint (closed cup)* (°C)	*Initial boiling point* (°C)
I	–	≤ 35
II	< 23	> 35
III	$\geq 23, \leq 60.5$	> 35

For Class 6, Poisonous (toxic) substances, there are grouping criteria for solids and liquids based on oral toxicity and dermal toxicity, both characterized by an LD_{50} value (the lethal dose at the 50% level) and for dusts and mists by an LC_{50} value (the lethal concentration at the 50% level) for a 1 hour exposure. For toxic vapours the grouping criteria are shown in Figure 23.1.

The *Code* gives a list of the dangerous goods most commonly carried. It also gives guidance on the assignment of a substance which is not in the list and which presents more than one hazard. The guidance is in the form of (1) a list of classes and divisions in order of precedence and (2) a precedence table.

The UN *Transport Code* gives detailed definitions of forms of packaging and specifies requirements for testing and marking.

23.3.3 European Road Carriage Agreement (ADR)

The classification for dangerous goods for transport by road given in the ADR is shown in Table 23.3. The classification is similar, but not identical, to that of the UN *Transport Code*.

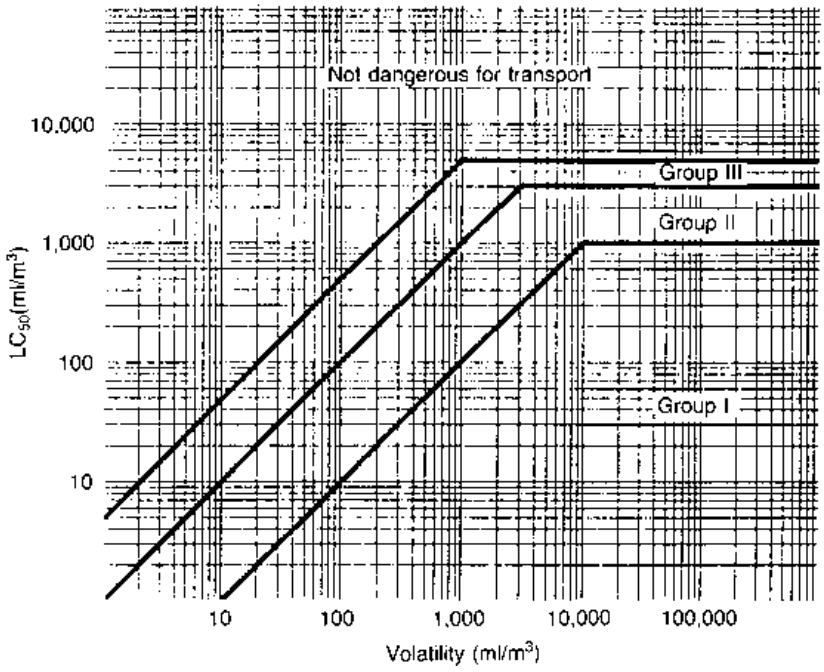


Figure 23.1 *UN* Transport Code: *grouping criteria for toxic vapours (United Nations, 1993; reproduced by permission)*

Table 23.3 *European Agreement for Road Transport (ADR): classification of substances*[a] *(Department of Transport, 1993a)*

Class 1	Explosive substances and articles
Class 2	Gas: compressed, liquefied or dissolved under pressure
Class 3	Flammable liquids
Class 4.1	Flammable solids
Class 4.2	Substances liable to spontaneous combustion
Class 4.3	Substances which give off flammable gases on contact with water
Class 5.1	Oxidizing substances
Class 5.2	Organic peroxides
Class 6.1	Toxic substances
Class 6.2	Repugnant substances and substances liable to cause infection
Class 7	Radioactive material
Class 8	Corrosive substances
Class 9	Miscellaneous dangerous substances and articles

[a] The classification given in the RID is identical with the above, except that very slightly different wording is used for Classes 4.3 (Substances which, in contact with water, emit flammable gases) and 6.2 (Infectious and repugnant substances).

A special feature of ADR is that the classes are either restrictive or non-restrictive. The restrictive classes are Classes 1, 2, 6.2 and 7. For a restrictive class, only the goods specifically listed may be carried and goods not listed are prohibited. For a non-restrictive class, some goods, although not specifically listed by name, may fall under one of the generic descriptions in the class, and are then carried according to the provisions which apply to that group, whilst other goods which display the dangerous properties of the class, but are not listed either specifically or generically, may be carried free of ADR. However, there are for non-restrictive Classes some goods which are prohibited.

ADR gives a further classification for Class 2, Gases, which is particularly relevant here. This is shown in Table 23.4.

23.3.4 International Rail Carriage Regulations (RID)

The classification for dangerous goods for transport by rail given in RID is the same as that shown Table 23.3, with the slight modification given in the footnote to that table.

23.3.5 CHIP Regulations 1993

Like the CPL Regulations which they replace, the Chemicals (Hazard Information and Packaging) Regulations 1993 (CHIP) deal with classification, packaging and labelling of chemicals.

There are three Health and Safety Executive (HSE) documents issued in support of these regulations. Guidance is given in L38 *Approved Guide to the Classification and Labelling of Substances and Preparations Dangerous for Supply* (the *Approved Classification and Labelling Guide*) (1993). L37 (1993)

Table 23.4 *European Agreement for Road Transport (ADR): classification of Class 2, Gases (Department of Transport, 1993a)*

A Subclasses of Class 2[a]		
A	Compressed gases having a critical temperature below −10°C	
B	Liquefied gases having a critical temperature of −10°C or above	
	(a) Liquefied gases having a critical temperature of 70°C or above	
	(b) Liquefied gases having a critical temperature of −10°C or above, but below 70°C	
C	Deeply refrigerated liquefied gases	
D	Gases dissolved under pressure	
E	Aerosol dispensers and non-refillable containers of gas under pressure	
F	Gases subject to special requirements	
G	Empty receptacles and empty tanks	
B First subdivision, mainly relating to pure/gas or mixture		
	Pure and technically pure gases	*Mixtures of gases*
A	1°	2°
B(a)	3°	4°
B(b)	5°	6°
C	7°	8°
D	9°	
Also		
E	10° aerosol dispensers; 11° non-refillable containers	
F	12° various mixtures of gases; 13° test gases	
G	14° empty receptacles and empty tanks, uncleaned	
C Second subdivision, relating to chemical properties		
(a)	Non-flammable	
(a t)	Non-flammable, toxic	
(b)	Flammable	
(b t)	Flammable, toxic	
(c)	Chemically unstable	
(c t)	Chemically unstable, toxic	

[a] These subdivisions are used in a hierarchy which may be illustrated by that of subclass A which is ordered: A; 1°; (a); (a t); (b); (b t); (c t); 2°; etc.

gives guidance on materials safety data sheets. The third document is the *Approved Supply List*, described below.

The CHIP Regulations cover both supply and conveyance. The supply provisions are designed to provide protection to those who handle dangerous substances, the conveyance provisions protection to those concerned with their conveyance.

The regulations distinguish between substances and preparations, the latter being mixtures of substances. They also distinguish in classification between supply and conveyance. Regulation 4 defines two approved lists. The *Approved Supply List* is given in *Information Approved for the Classification and Labelling of Substances and Preparations for Supply* and the *Approved Carriage List* is given in *Information Approved for the Classification and Labelling of Substances and Preparations for Carriage*.

Regulation 5 requires that a substance or preparation dangerous for supply should not be supplied unless it meets the requirements of this regulation, which include that it is in the *Approved Supply List*, that it is a new substance classified in accordance with the Notification of New Substances Regulations 1982, or that it is classified in accordance with Schedule 1 of the CHIP regulations. Regulation 6 requires that the supplier should provide a safety data sheet. Regulation 7 requires that a substance or preparation dangerous for carriage should not be carried unless it has been classified by reference to the *Approved Carriage List* in the manner specified in the regulation.

Regulation 8 gives requirements for the packaging of substances or preparations dangerous for carriage or supply. These requirements cover three main points. The package should be designed, constructed, maintained and closed so as to prevent the leakage of the contents when the overall package is subjected to normal handling. Any packaging materials likely to come into contact with the substance should be compatible with it. The closure on a container which is repeatedly reused should be designed so that even after repeated use it will not leak. These requirements are essentially similar to those of the CPL Regulations.

Regulation 9 gives requirements for the labelling of substances and preparations dangerous for supply. These include the name and address of the supplier, information about the substance, symbols and risk and safety phrases. Regulation 10 gives requirements for the labelling of substances and preparations dangerous for carriage. These include the name and address of the supplier and the hazard warning sign.

Schedule 1 of the regulations gives three bases of classification: (1) physico-chemical properties, (2) health effects, and (3) environmental effects. Classification on the basis of physico-chemical properties is made using the headings: (1) explosive, (2) oxidizing, (3) extremely flammable, (4) highly flammable and (5) flammable. Classification on the basis of health effects is made under the headings: (1) very toxic, (2) toxic, (3) harmful, (4) corrosive, (5) irritant, (6) carcinogenic, (7) mutagenic and (8) teratogenic.

Schedule 2 gives the indications and symbols for substances and preparations dangerous for supply and Schedule 3 the hazard warning signs for substances and preparation dangerous for carriage. Schedule 4 gives classification provisions for preparations dangerous for supply and Schedule 5 gives those for pesticides. Schedule 6 lists the headings under which particulars are to be provided in safety data sheets.

L38 gives guidance particularly on: (1) the classification by physico-chemical properties, health effects and environmental effects; and (2) labelling and risk and safety phrases. For the classification of substances the data necessary are essentially those of the base set given in the Notification of New Substances Regulations 1982. The guide refers particularly to the test methods of EC Directive 84/449/EEC.

With regard to labelling, L38 gives two separate sets of formal phrases: the risk phrases and the safety phrases. A risk phrase which figures prominently in occupational hygiene is R45: May cause cancer.

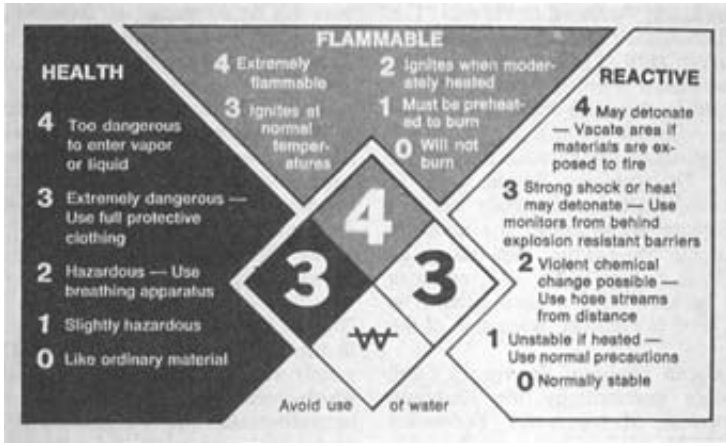


Figure 23.2 *NFPA 704 diamond (National Fire Protection Association, 1990). (Copyright © 1990 National Fire Protection Association Quincy, MA 02269. This warning system is intended to be interpreted and applied only by properly trained individuals to identify fire, health and reactivity hazards of chemicals. The user is referred to a certain limited number of chemicals with recommended classifications in NFPA 49 and NFPA 325M which would be used as a guideline only. Whether the chemicals are classified by the NFPA or not, anyone using the 704 system to classify chemicals does so at their own risk.)*

Another risk phrase which occurs frequently in L38 is R48: Danger of serious damage to health by prolonged exposure. L38 gives detailed guidance on when R48 should be used. Other typical risk phrases are R23: Toxic by inhalation, and R35: Causes severe burns. Some typical safety phrases are S15: Keep away from heat, S22: Do not breathe dust, and S29: Do not empty into drains.

Detailed guidance on packaging is given in COP 40, an ACOP to the CPL Regulations. Aspects covered include: normal handling, dropping, stacking, abrasion and vibration of packaging and weather effects on packaging; packaging of liquids and venting of packages; and repeated use of packages.

A major feature of this code is the packaging of organic peroxides. It gives in Appendix A1 a list of such peroxides, in Appendix A2 a list of special provisions for these peroxides and in Appendix A3 a list of recommended packagings. It also gives in Appendix B criteria for the packaging of organic peroxides not listed in Appendix A, utilizing the concept of the self-accelerating decomposition temperature.

As with classification, so with labelling a distinction is made between supply and conveyance. In general, for supply there should be labelling on each discrete layer of packaging, while for conveyance labelling is required only on the other layer.

For supply the particulars to be shown are:

(1) designation of the substance;
(2) indication(s) of the general nature of risk and the corresponding symbols;
(3) risk phrases;
(4) safety phrases;
(5) name and address of the manufacturer, importer, wholesaler or other supplier.

For conveyance the particulars are:

(1) designation of the substance;
(2) substance identification number;
(3) hazard warning sign;
(4) additional information, covering such matters as –
  (a) nature of the dangers,
  (b) advice on first aid,
  (c) action in case of fire,
  (d) measures to deal with any spillage,
  (e) instructions about any safety equipment;
(5) name and address or telephone number of consignor or expert from whom advice on the hazard is available.

The CHIP Regulations are designed to be consistent with the international codes such as the UN *Transport Code*, ADR, RID and the *IMDG Code*.

23.3.6 Hazard warning symbols and signs

The hazard warning labels, i.e. signs and symbols, are international. The UN *Transport Code* gives specimen labels. Hazard warning signs for supply (brown) and symbols for carriage (multi-coloured) are given in the CHIP Regulation 1993. Hazard warning panels for road tankers are given in the Road Traffic (Carriage of Dangerous Substances in Road Tankers and Tank Containers) Regulations 1992.

Plate 21 shows typical hazard warning symbols for supply, Plate 22 shows hazard warning signs for carriage and Plate 24 shows hazard warning panels.

23.3.7 HAZCHEM system

The Chemical Industries Association (CIA) operates the HAZCHEM scheme described in *Hazard Identification—*

A Voluntary Scheme for the Marking of Tank Vehicles and Dangerous Substances (1975/X).

HAZCHEM code panels are illustrated in Plate 24. The top panel shows the HAZCHEM code number (2PE), the UN classification number (1230), the emergency telephone number and the hazard warning sign.

The HAZCHEM guide is shown in *Plate 23*. It gives information under the following letter code: A, emergency action code; B, substance identification number; C, hazard warning sign; D, specialist advice; and E, evacuation. The first character in the code number refers to A, the emergency action code. The numbers 1, 2, 3 and 4 refer to the fire fighting methods to be used. The first letter P, R, S T or W, X, Y, Z, refers to the spillage action to be taken. The second letter E is added where there is need to consider evacuation of the area.

There is also a European Transport Emergency Card, or TREMCARD, system operated by the European Council of the Chemical Manufacturers Federation (CEFIC) (CIA/l). A TREMCARD is shown in Plate 25.

23.3.8 US arrangements

For the USA accounts of controls on classification, packaging and labelling of dangerous substances are given in the *NFPA Handbook* (Cote and Linville, 1986) and by Bierlein (1984). The regulating authority is the Department of Transportation (DOT).

NFPA 704 provides a labelling system based on the classification system given in that code. The National Fire Protection Association (NFPA) diamond is shown in Figure 23.2.

The DOT has a placard and labelling system. The system uses the United Nations (UN) hazard diamonds. Details of the system are given in the *NFPA Handbook*.

23.4 Transport Containers

23.4.1 Regulatory controls and codes

The containers used for transport, whether fixed on a vehicle or multi-modal, are the subject of detailed requirements in the UN *Transport Code*, ADR, RID and the *IMDG Code*. The general nature of the requirements for transport containers may be illustrated by considering those given in the UN *Transport Code* and in the ADR for road transport.

23.4.2 Types of container

The types of container used in the transport of dangerous goods include: (1) tanks fixed to road vehicles and rail cars; (2) multi-modal tank containers, which can be transported by several different modes of transport; and (3) intermediate bulk containers. There are also demountable tanks, which differ from tank containers in that they are not intended to be loaded and unloaded whilst fully charged.

The UN *Transport Code* defines a tank container as a tank having a capacity of not less than 0.45 m^3 whose shell is fitted with the items of service equipment and structural equipment necessary for the transport of dangerous liquids.

It defines an intermediate bulk container (IBC) as a rigid, semi-rigid or flexible packaging having a capacity of not more than 3 m^3 which is designed for mechanical handling and is resistant to the stresses produced in handling and transport, as determined by tests. Excluded from this definition are the forms of packaging dealt with in Chapter 9 of the code, which covers items having a mass of less than 400 kg or a capacity of less than 0.45 m^3.

Tank containers are treated in the UN *Code* in terms of requirements for pressure vessels. IBCs are treated rather in terms of the requirements for packaging, with emphasis on tests for such packaging. There are pressure test requirements, however, for certain metal IBCs such a drums.

The ADR contains provisions for fixed tanks, or tank vehicles, and for tank containers.

23.4.3 Tank containers

In the UN *Transport Code* transport containers are dealt mainly with in Chapter 12 on multi-modal tank transport, which covers tank containers for Classes 3–9 and for non-refrigerated liquefied gases, and Chapter 17 on multi-modal tank containers for refrigerated liquefied gases. The treatment is under the following broad headings: (1) general requirements, (2) cross-sectional design, (3) minimum shell thickness, (4) service equipment, (5) bottom opening, (6) safety relief, (7) pressure relief devices, (8) setting and (9) capacity.

The treatment of transport containers in the ADR is mainly in Appendix A6 on intermediate bulk containers and in Appendices B1a–c, dealing with tanks other than tank containers, tank containers, and tanks made of reinforced plastics, respectively. The treatment is under the headings: (1) general scope and definitions; (2) construction; (3) items of equipment; (4) type approval; (5) tests, (6) marking; and (7) operation.

23.4.4 Road tankers

The other main type of tank of interest here is fixed tanks on road tankers and rail tank cars. The general principles are similar for the two modes of transport and it is road tankers which are now considered.

The requirements for road tankers, or tank vehicles, are treated in detail in the ADR. In the account which follows the provisions quoted relate to the general requirements for tank vehicles. For some classes there are also specific requirements.

23.4.5 Tank shell construction

The mechanical design of the tank shell on a tank vehicle is treated in detail in the ADR. The shell should be designed and constructed in accordance with a suitable code. The ADR gives certain minimum requirements covering, among other things, (1) the material of construction, (2) the minimum wall thickness, (3) the design pressure and test pressure, and (4) the transport shocks.

23.4.6 Material of construction

The general requirement of the ADR is that the shell of a tank vehicle should be made of a suitable metallic material which is resistant to brittle fracture and stress corrosion cracking between −20°C and 50°C, except where another temperature range is prescribed for a particular class.

The usual material of construction for the shell is mild steel. Lined mild steel is also used. The usual linings are

plastics and rubber. In this case it is necessary to maintain the lining carefully, especially at the joints.

Other materials are used for tanks for particular chemicals. For example, aluminium alloy is utilized for hydrogen peroxide.

23.4.7 Minimum wall thickness

ADR gives the following formula for the calculation of the thickness of the cylindrical wall of the shell of a tank vehicle and of the ends and cover plates:

$$e = \frac{PD}{20\sigma\lambda} \qquad [23.4.1]$$

where D is the internal diameter of the shell (mm), e is the thickness of the metal (mm), P is the calculation pressure (bar), σ is the permissible stress (N/mm^2) and λ is a coefficient, not exceeding unity, which allows for any weakening due to welds.

There is also a minimum wall thickness. For a shell not exceeding 1.8 m diameter this minimum thickness is 5 mm for mild steel, and for one of larger diameter it is 6 mm. For other metals an equivalent thickness is applicable, determined from a formula based on the general relation

$$e_1 = e_0 \left(\frac{R_{m0} A_0}{R_{m1} A_1} \right)^{\frac{1}{3}} \qquad [23.4.2]$$

where A is the fractional minimum elongation of the metal on fracture under tensile stress, R_m is the minimum tensile strength, and subscripts 0 and 1 denote mild steel and the metal under consideration, respectively.

23.4.8 Design pressure

For the design pressure of the shell of a tank vehicle the general provisions of the ADR define four categories of duty. The fourth covers shells for use with substances having a vapour pressure of more than 1.75 bara at 50°C. For this case the calculation pressure should be 1.3 times the filling or discharge pressure, but in any case not less than 4 barg.

23.4.9 Transport shocks

The shell, and its fastenings, on a tank vehicle are required by the general provisions of the ADR to withstand the following forces:

(1) In the direction of travel: twice the total mass.
(2) At right angles to the direction of travel: the total mass.
(3) Vertically upwards: the total mass.
(4) Vertically downwards: twice the total mass.

23.4.10 Tank equipment

The ADR general provisions detail the equipment which should be provided on the shell of a tank vehicle. This includes shut-off devices on bottom-discharge shells and pressure relief devices.

A bottom discharge should be equipped with two mutually independent shut-off devices. The first should be an internal stop valve fixed directly to the shell and the second a sluice valve, or equivalent device, mounted in series, one at each end of the discharge pipe socket. In addition, the openings of shells should be capable of being closed by screw-threaded plugs, blank flanges or equivalent devices.

The internal shut-off valve should be operable from above or below, and its setting (whether open or closed), should if possible be verifiable from the ground. The valve should continue to be effective in the event of damage to the external control.

23.4.11 Pressure relief

The general provisions of the ADR require that a shell for carriage of a liquid with a vapour pressure exceeding 1.1 bara at 50°C should either be fitted with a safety valve or be hermetically sealed. A hermetically sealed shell is one with hermetically closed openings and without a safety valve, bursting disc or similar device, or one fitted with a safety valve preceded by a bursting disc.

The special provisions for Class 2, gases, state that a shell for gases in 1° to 6° and 9° may be fitted with safety valves. But they also state that for carriage of toxic gases in 1° to 9° a shell should not have a safety valve unless it is preceded by a bursting disc. In this latter case the arrangement should be satisfactory to the competent authority. These provisions also state that for shells intended for carriage by sea the provisions of ADR do not prohibit the fitting of safety valves conforming to the regulations of the *IMDG Code*.

The fitting of a pressure relief valve to a road tanker is not a straightforward matter. The topic is discussed by Hawksley (1990 LPB 91), who points out that it cannot be assumed that the fluid to be relieved will necessarily be vapour; in some cases with the tanker lying on its side the fluid may be liquid. He considers the problems which this poses.

23.4.12 Filling ratio

The general provisions of the ADR contain a number of formulae for the degree of filling (DF). These are of the general form

$$\mathrm{DF} = \frac{\chi}{1 + \alpha(50 - t_F)} \qquad [23.4.3]$$

with

$$\alpha = \frac{d_{15} - d_{50}}{35 \times d_{50}} \qquad [23.4.4]$$

where d_{15} and d_{50} are the densities of the liquid at 15°C and 50°C, respectively, t_F is the mean temperature of the liquid at the time of filling (°C), α is the mean coefficient of cubical expansion of the liquid between 15°C and 50°C and χ is a proportion (%) which has values dependent on (1) the nature of the fluid and (2) the pressure relief arrangements, these values ranging between 95% and 100%.

23.5 Road Transport

23.5.1 Regulatory controls and codes

At the international level, codes for the road transport of dangerous goods are the UN *Transport Code* and the ADR.

In the UK, road transport is governed by three principal sets of regulations. The first set is the Chemical (Hazard Information and Packaging) Regulations 1993 (CHIP), which cover these aspects as they apply to road transport. These regulations, and the

associated ACOPs and guidance, have been described in Section 23.3.

The second set are the Road Traffic (Carriage of Dangerous Substances in Packages) Regulations 1992 (PGR). The regulations deal with: the design, construction and maintenance of vehicles; the marking of vehicles; loading, stowage and unloading; precautions against fire and explosion; information to be provided to the operator; information for, instructions to and training of drivers; supervision of parked vehicles; and information for the police. Regulation 11 places limitations on the carriage of certain substances. It contains requirements that an organic peroxide or flammable solid subject to self-accelerating decomposition be kept below its control temperature.

The third set of regulations are the Road Traffic (Carriage of Dangerous Substances in Road Tankers and Tank Containers) Regulations 1992 (RTR). The regulations deal with: the construction, maintenance and testing of tankers and tank containers; the marking of vehicles with hazard warning panels; loading, filling and securing of closures; information to be provided to the operator; information to be carried with the vehicle; precautions against fire and explosion; information for, instructions to and training of drivers; parking of vehicles and their supervision when parked; and information for the police.

Both the PGR and RTR give definitions of dangerous substances, referring in particular to the *Approved List*. The PGR also contain a schedule which gives criteria by which to determine whether a substance not in the list is to be classed as a dangerous substance.

The regulations which preceded these two sets of road traffic regulations, PGR 1993 and RTR 1993, namely PGR 1986 and RTR 1981, were supported by a number of ACOPs and guidance documents. The ACOPs are COP 11 *Operational Provisions of the Dangerous Substances (Conveyance by Road in Road Tankers and Tank Containers) Regulations 1981* (HSE, 1983); COP 14 *Road Tanker Testing: Examination, Testing and Certification of the Carrying Tanks of Road Tankers and Tank Containers used for the Conveyance of Dangerous Substances by Road (in support of SI 1981 1059)* (HSE, 1985); and COP 17 *Notice of Approval of the Operational Provisions of the Road Traffic (Carriage of Dangerous Substances in Packages etc.) Regulations 1986 by the Health and Safety Commission* (HSE, 1987). The guidance is HS(R) 13 *Guide to the Dangerous Substances (Conveyance by Road in Road Tankers and Tank Containers) Regulations 1981* (HSE, 1981) and HS(R) 24 *Guide to the Road Traffic (Carriage of Dangerous Substances in Packages etc.) Regulations 1986* (HSE, 1987).

These documents are currently in the process of being updated, with a single L series document replacing both ACOPs and the guidance. A single document will replace COP 11 and HS(R) 13, another will replace COP 14 and a third will replace COP 17 and HS(R) 24.

The design and construction of road tankers is covered in the following documents: L16 *Design and Construction of Vented Non-pressure Road Tankers used for the Carriage of Flammable Liquids* (HSE, 1993); L17 *Design and Construction of Road Tankers used for the Carriage of Carbon Disulphide* (HSE, 1993); L18 *Design and Construction of Vacuum Insulated Road Tankers used for the Carriage of Deeply Refrigerated Gases* (HSE, 1993); and L19 *Design and Construction of Vacuum Operated Road Tankers used for the Carriage of Hazardous Wastes* (HSE, 1993).

The road transport of explosives is covered by the Road Traffic (Carriage of Explosives by Road) Regulations 1989. The associated ACOP is COP 36 *Carriage of Explosives by Road* (HSE, 1989).

23.5.2 Hazard scenarios

The bulk of hazardous materials transported by road are carried as liquids or liquefied gases in road tankers. The main types of road accident associated with these are leaks due to tank puncture resulting from a collision or overturning or due to failure or maloperation of the tank equipment. Other causes of loss of containment are tank rupture due to overfilling, overheating or a defect and due to fire.

If the tank is ruptured by overfilling or overheating, a physical explosion may occur, giving rise to a blast wave and to missiles.

Material released from the tank by whatever cause may be flammable or toxic and in vapour or liquid form. A release of flammable vapour will form a vapour cloud which may ignite to give a flash fire or vapour cloud explosion. A flammable liquid spill may ignite to give a pool fire or flowing liquid fire. A toxic material will give a toxic gas cloud or toxic liquid spill.

A fire at the tank itself may cause rupture of the tank and, if the tank contains flammable liquid, may lead to a boiling liquid expanding vapour explosion (BLEVE), with its associated fireball. Road tankers do not, however, suffer BLEVEs as commonly as rail tankers, because there is not the torch effect from relief valves on other tanks which occurs in rail crashes.

Other hazardous materials are solids which are carried in goods vehicles. These include explosives and related substances. With these there is therefore the hazard of explosion.

There are several characteristics of road transport which bear on the nature of the hazard. The vehicle is moving through an environment over which the driver has relatively little control. If there is an accident, it may occur at a variety of points along the route with very different vulnerabilities. On the other hand, the quantity carried is limited, and it may be possible to move the vehicle to a less vulnerable location.

One important aspect of vulnerability is the number of people exposed at a particular location. The extent and composition of the population exposed varies widely with the location. Another aspect is the susceptibility to environmental pollution at that point. A road accident may pose a threat not only to life but also to the environment.

A feature of road accidents is that access for the emergency services is generally relatively easy compared with rail. On the other hand, the accessibility of a road accident increases the likelihood that spectators will gather.

23.5.3 Road tanker design

Requirements for the design of road tankers are given in the Road Traffic (Carriage of Dangerous Substances in Road Tankers and Tank Containers) Regulations 1992 (RTR). An outline of these requirements has been given

in Section 23.5.1. Associated guidance is given in L16 for flammable liquids and L18 for deeply refrigerated liquids.

The RTR are essentially a set of goal-setting regulations and do not specify matters such as wall thickness or overpressure protection. In particular, the requirements of the RTR for design and for testing and examination, given in Regulations 6 and 7(1), respectively, are very general, and much less detailed than those given in the ADR. The RTR states in Regulation 8(5) that the aforementioned regulations do not apply to the carrying tank of a road tanker or to a tank container where that tank and its fittings comply with the ADR, RID or the IMDG *Code*. In other words, compliance with the ADR is in effect one way of meeting the requirements of the RTR.

There are also several industry codes which deal with the design and/or operation of road tankers. These include *Safe Handling and Transport of LPG in Bulk by Road* by the (LPGITA, 1974 COP2), *Code of Practice for Road Tank Vehicles Equipped with Bottom Loading and Vapour Recovery* (IP, 1987), *Road Transport of Dangerous Substances in Bulk* (CIA, 1990 RC26) and *Steel Containers for the Carriage of Hazardous Materials* (CIA, 1991 RC37).

For the more hazardous substances it is common practice to use top rather than bottom connections and to provide the vehicle with additional features such as side protection.

A road tanker for chlorine is shown in Plate 30.

23.5.4 Carriage tank fittings

The provision of suitable carriage tank fittings can make a major contribution to minimizing any loss of containment, both in road accidents and in loading and unloading. Good practice with respect to such provision is illustrated by the features specified in the ADR, some of which have been described in Section 23.4.

One particular feature is the arrangements for protection against overpressure. For flammables, the practice is to fit pressure relief. HSE guidance is given in L16, and L18. L16 for flammable liquids, requires each tank to be fitted with pressure relief devices, which it specifies. L18, for non-toxic, deeply refrigerated gases, likewise requires pressure relief devices on each tank, and specifies them.

For toxics, such provision is more controversial. In COP 38 on transportable gas containers the HSE state that containers for toxic fluids should not normally be fitted with pressure relief devices.

23.5.5 Road tanker operation

The RTR also contain requirements for the operation of road tankers, which reflect some of the elements of good practice.

The documentation supplied should contain the information necessary for all the parties concerned, which include the consignee, the driver, the police and the fire service.

The driver should be well trained in and provided with the information which he requires. The training should cover: loading and unloading operations, including precautions against overfilling and measures to secure closures; arrangements at lorry stopover points; and handling emergencies, including both spillage and fire.

The vehicle, the carriage tank and its fittings need to be maintained to a high standard.

23.5.6 Filling ratio

It is essential that a tank should not be overfilled, with the consequent hazard of rupture due to expansion of the liquid. The permissible extent of filling is specified in terms of the filling ratio.

Guidance is given in the BS 5355: 1976 *Filling Ratios and Developed Pressures for Liquefiable Gases and Permanent Gases*. This standard, as amended in 1981, defines the filling ratio as:

> The ratio of the mass of gas introduced into a container to the mass of water (water capacity) at 15°C that fills the container fitted as for use, i.e. complete with valve, dip tube, float, etc. as necessary.

BS 5355 gives in Appendix A formulae for the filling ratio (FR). It distinguishes between a low pressure liquefiable gas, which has a critical temperature between −10°C and 70°C, inclusive, and a high pressure liquefiable gas, which has a critical temperature above 70°C. For single components, the filling ratio formulae are of the general form

$$\mathrm{FR} = \frac{\chi\rho_1(1 - C/100)}{\rho_w} \qquad [23.5.1]$$

where C is the confidence limits on the value of the liquid density (%), ρ_1 is the density of the liquid, ρ_w is the density of water and χ is a parameter which has the value 0.97 for low pressure liquefiable gases and 0.98 for high pressure liquefiable gases. The liquid density is to be evaluated at the appropriate reference temperature.

The standard also give values of the filling ratio in tabular form for a large number of gases.

23.5.7 Reference temperature

The reference temperature is the assumed maximum temperature which the tank contents could reach during carriage. It is used to determine the filling ratio and also the developed pressure.

BS 5355: 1976 gives reference temperatures for the UK and also information which allows reference temperatures to be determined for other parts of the world. It classifies areas according to the maximum shade temperature. The UK is classified as a climatic area with a shade temperature ≤35°C. In addition to Class UK, there are Classes A–E, with maximum shade temperatures of 37.5, 42.5, 47.5, 52.5 and >52.5°C, respectively.

Then for the UK the reference temperature for container volumes (V) over 1 m^3 are as follows:

Type of contents	*Reference temperature for filling ratio (°C)*		*Reference temperature for developed pressure (°C)*	
	V=1–5 m^3	$V>5$ m^3	V=1–5 m^3	$V>5$ m^3
Low pressure liquefiable gases	42.5	38	47.5	42.5
High pressure liquefiable gases	–	–	50	45

For low pressure liquefiable gases in winter, the standard gives a relaxation in reference temperature for filling ratio for volumes exceeding 5 m^3.

The choice of reference temperature is a very debatable subject. If a single reference temperature is used, simplicity is achieved, but the temperature selected has to be much higher than is necessary and economic for a large proportion of cases. Discussions of this point are given in the Home Office *Containers Report* and by A.W. Clarke (1971b). The latter states that reference temperatures as high as 65°C have been used in international codes.

The reference temperatures provide overall guidelines, but it is necessary also to observe any requirements of international transport and of the country of delivery.

23.5.8 Hazardous materials

For a given mode of transport there are some hazardous materials which may not be conveyed. Road transport is a case in point. Writing in 1971, A.W. Clark (1971b) gave the following list of substances prohibited for road transport in West Germany:

Class 2 Gases: chlorine, hydrogen bromide, hydrogen chloride, hydrogen fluoride, hydrogen sulphide, phosgene, sulphur dioxide.
Class 3 Flammable liquids: carbon disulphide.
Class 6 Poisons: acetone, cyanohydrin, acetonitrile, acrylonitrile, allyl alcohol, allyl chloride, aniline, epichlorohydrin, lead alkyls, organophosphorus compounds.
Class 8 Corrosives: bromine, fluoboric acid, hydrazine, liquid acid halides and liquid chlorides which give off acid fumes in contact with moist air (e.g. antimony pentachloride).

For certain chemicals which are transported by road special measures are required. These include:

(1) substances liable to polymerization;
(2) substances carried fused;
(3) hydrogen peroxide;
(4) organic peroxides;
(5) sulphur trioxide;
(6) bromine;
(7) lead alkyls.

Some chemicals, such as butadiene or ethylene oxide, have a tendency to polymerize. It is essential to prevent polymerization from starting, because if polymerization occurs heat is evolved and the reaction speeds up. One method of prevention is the use of an insulated tank, but this is increasingly being replaced by the alternative method, which is the use of polymerization inhibitors.

Some substances which are solids at ambient temperature, such as sulphur, phosphorus, alkali metals and naphthalene, are often carried in fused form in overdesigned and insulated tanks.

High strength hydrogen peroxide is transported in aluminium or special steel tanks. Materials which could react with the peroxide such as wood or valve lubricants are excluded from the vehicle. A water tank is carried to deal with any accident.

Organic peroxides are a somewhat similar case. They are sometimes carried in refrigerated insulated tanks to minimize the hazard due to their instability.

Sulphur trioxide is a solid at ambient temperatures and is carried heated in overdesigned and insulated tanks. It is stabilized to present polymerization. Bromine is usually transported in lead-lined steel tanks. Lead alkyls are carried in overdesigned and externally protected tanks.

23.6 Road Transport Environment

23.6.1 Road network and vehicles

The assessment of major hazards arising in the road transport of hazardous materials requires the use of a wide range of data on the road transport environment.

The road transport environment varies somewhat from one country to another. Accounts relevant to the UK have been given by Appleton (1988 SRD R474) and P.A. Davies and Lees (1992), and accounts relevant to North America have been given by Glickman (1988), Harwood and Russell (1989), Harwood, Russell and Viner (1989), Harwood, Viner and Russell (1990), Steward and van Aerde (1990a) and Gorys (1990).

As in hazard assessment generally, two situations can arise with respect to the estimation of the frequency of particular accident scenarios. Either it is possible to estimate the frequencies of these scenarios from historical data, or it is necessary to synthesize the frequencies, by methods such as modelling or fault tree analysis.

Thus for scenarios such a release of materials which are transported in large quantities (e.g. gasoline and LPG) it may well be possible to obtain historical data. For other scenarios, such as a release of chlorine or an explosion of explosives during transport, it is much more difficult. Moreover, even where historical data exist, it may still be necessary to resort to modelling for reasons such as the need to adapt the data to the particular assessment or to explore the effect of possible mitigatory measures.

As will become apparent from the data given below, a large proportion of incidents involving hazardous materials are not due to traffic accidents, but to other causes. The prime concern here is with incidents which occur during transport rather than during loading and unloading or in temporary storage, but some of the data sets also cover the latter.

Hazardous goods are taken here to be goods defined as such under the United Nations classification and regulated by the Classification, Packaging and Labelling Regulations 1984 (CPL). These hazardous materials are mainly flammable and/or toxic liquids and liquefied gases, reactive chemicals and explosives.

The principal source of information on road transport and on road accident statistics is the Department of Transport (DTp). Other important sources are the Home Office and the Transport and Road Research Laboratory (TRRL), which is part of the Department of the Environment (DoE).

Unfortunately, as so often happens, there are difficulties in relating information from one source to that from another. For example, DTp statistics are for heavy goods vehicles (HGVs) with unladen weights of not less than 1.5 te, whereas the principal TRRL study of HGV fatal accidents deals with HGVs with unladen weights not less then 3 te.

Road network

There are two classifications of roads used in Britain. Roads are generally classified as trunk, principal, secondary, etc., whilst in accident statistics roads are described as A class, B class, and 'other'. Broadly speaking, trunk and principal roads are equivalent to A class roads, whilst secondary roads are equivalent to B class and 'other' roads (P.P. Scott, 1983). The length of the road network (km) in Great Britain in 1973 was given by H.D. Johnson (1981) as follows:

Length of road (km)						
BUA[a]			*Non-BUA*			
Trunk/ principal	*Class II and below*[b]	*Total*	*Trunk/ principal*	*Class II and below*[b]	*Total*	*Motorways*
13 874	117 052	130 926	32 383	163 587	195 970	1752

[a] BUA: built-up area
[b] Of these totals, Class II roads are 8746 km in BUAs and 19 643 km in non-BUAs.

Heavy goods vehicles

Vehicles may be classed as heavy goods vehicles (HGVs), light goods vehicles (LGVs), cars, and motor cycles (MCs). HGVs may be subdivided according to the number of axles. The vast majority of hazardous materials are carried in HGVs. The most common HGV is the rigid two-axle vehicle.

The mass unladen of a typical two-axle HGV is some 7.5 te and that of a typical three-axle HGV is some 11.5 te, while that of an LGV is some 1.5 te. The maximum load of a two-axle HGV is some 12 te. Approximately 50% of HGVs carry full load and 25% are empty, with the remainder carrying part loads. The load of an LGV is some 1.5 te.

A total of 435 000 HGVs were registered in 1986 (DTp, 1987b). The distribution of HGV weights for 1985 (JMP Consultants, 1986) was

Gross vehicle weight (te)	*Proportion of vehicles* (%)
< 20	70
20–22	3
22–24	3
24–26	2
26–28	2
28–30	4
30–32	6
32–34	4
34–36	2
36–38	3
> 38	1

Figure 23.3 shows some principal heavy goods vehicles together with their classifications.

Distances travelled

The journeys travelled by HGVs in 1986 are shown in Table 23.5, Section A, by body type and road type. HGVs travelled a total of 221×10^8 km (DTp, 1987b). The average annual distance travelled per vehicle is thus 50 800 km ($221 \times 10^8/435\,000$). Section B of the table gives a breakdown of the HGV distances travelled by road class.

Speed in built-up areas

The severity of an accident depends on the speed of the vehicle(s). Of particular interest is the speed of vehicles in built-up areas (BUAs). Work on this has been done by the TRRL (N. Duncan, 1987). Their data for the speeds of good vehicles generally, LGVs as well as HGVs, are:

Time of day	*Average speed* (mph)	
	Small towns	*Large towns*
Peak period	13.1	20.5
Off-peak period	14.9	23.6

Table 23.5 *Road transport environment in Great Britain: journeys by heavy goods vehicles in 1986 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Distances travelled by body type and road type

HGV type	*Distance* ($\times 10^8$ km)		
	All speed limits	*Non-BUR*[b]	*BUR*
Rigid	152	103	49
Articulated	65	58	7
Total[a]	221	165	56

B Proportion of distance travelled on each road class

Road class	*Proportion of vehicles* (%)	
	Non-BUR[c]	BUR
A	87.0	61.0
B	6.0	11.5
Other	7.0	27.5
Total	100	100

[a] Figures for rigid and articulated vehicles are for defined axle configurations. Total includes cases where the axle configuration was not reported.
[b] BUR, built-up road. Non-BUR includes motorways.
[c] Non-BUR excludes motorways.

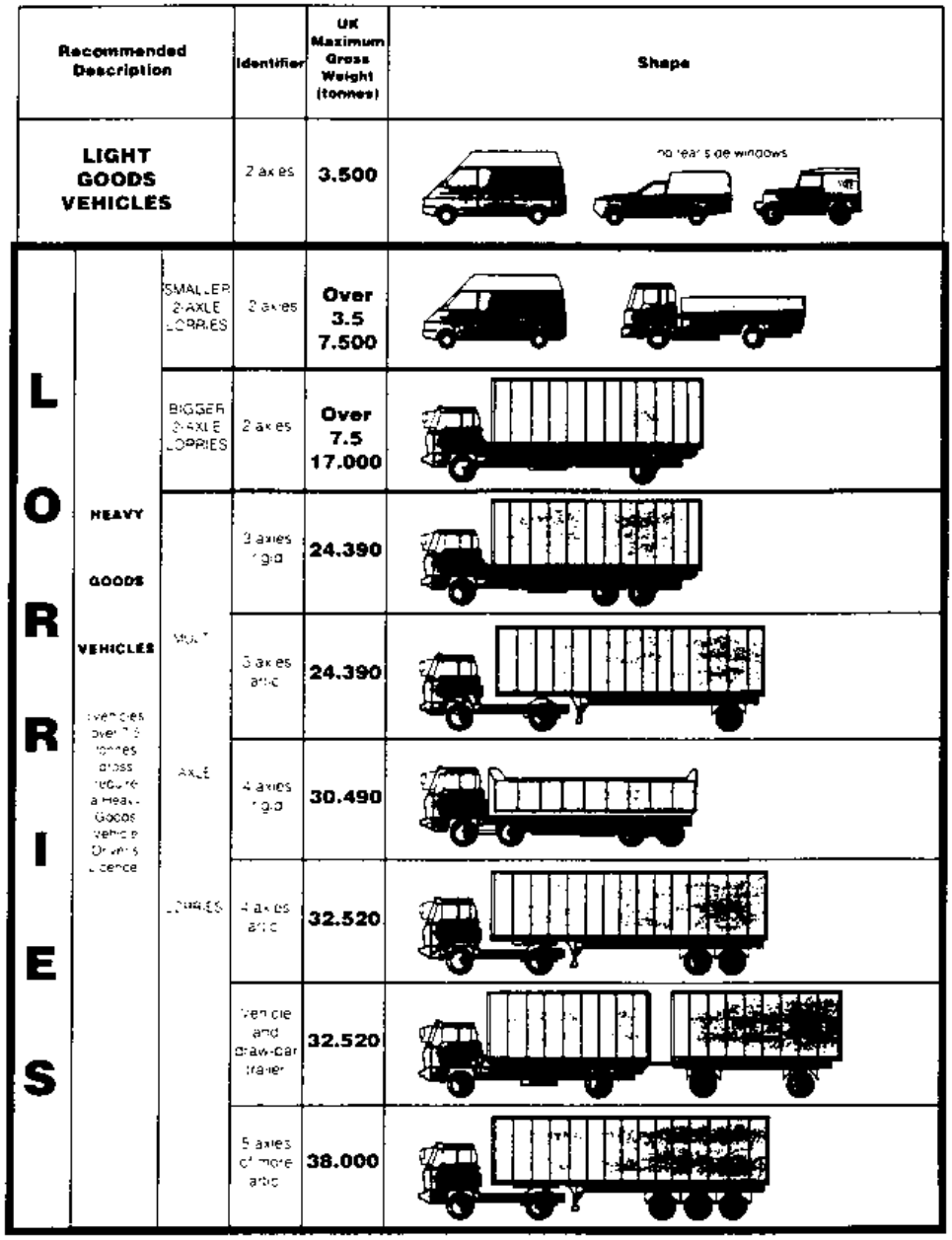


Figure 23.3 *Some principal goods vehicles*

The figures refer only to the time when the vehicle is actually moving, the time spent stationary is discounted.

With regard to the distribution of speeds, the assumptions made by TRRL are that the normal distribution applies and that the standard deviation is $\frac{1}{5}$ of the mean. Using these assumptions estimates may be made of the probability that a vehicle may be travelling at a particular speed.

More specific data on vehicle speeds at the moment of impact may be obtained from tachograph records, as described below.

HGVs conveying hazardous materials (HGV/HMs)

Some estimates are now made for HGVs conveying hazardous materials (HGV/HMs) in Great Britain.

Table 23.6 *Road transport environment in Great Britain: tanker capacities and movements for four hazardous materials (Advisory Committee on Dangerous Substances, 1991) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

A Tanker capacities

Substance	*Tank capacity* (te)
Motor spirit	20–25
LPG	15
Ammonia	15
Chlorine	17

B Tanker movements

	Motor spirit	*LPG*	*Ammonia*	*Chlorine*
Total loaded movements (loaded tanker km/year)	82×10^6	19.54×10^6	632 233	1 121 358
Total loaded journeys (loaded tanker journeys/year)	1.3×10^6	63 667	2974	9871
Average loaded journey (km)	64	307	213	114

It has been estimated by Kletz (1986j) that in 1986 there were some 14 000 road tankers in operation. The authors have confirmed that this approximate figure is still valid. Kletz also gives the annual distance travelled per tanker as 60 000 miles (96 500 km).

There are, in addition, HGVs other than tankers carrying hazardous materials. The number of such vehicles which at some time transport hazardous materials may be quite large, but what matters in the present context is the number of equivalent 'full-time' vehicles. There appears to be no reliable source of information for this figure. An estimate has therefore been made. The data for hazardous cargoes in the USA given in Section B of Table 23.20 (see below) indicate that the ratio of non-tank truck to tank truck HGV/HMs is about 0.6. Those given in Section B of Table 23.18 (see below) for significant spillages indicate that the ratio of non-tank truck to tank truck HGV/HM spillages is about 0.9. The former figure is regarded as a better guide. A roadside survey conducted by the authors is consistent with this estimate. The ratio of 0.6 is used for Great Britain also, which yields:

No. of tanker HGV/HMs = 14 000
No. of non-tanker HGV/HMs = 0.6 × 14 000 = 8400
No. of HGV/HMs = 14 000 + 8400 = 22 400

Distance travelled by HGV/HMs
For the distance travelled by HGV/HMs, loaded and unloaded:

Distance travelled by individual vehicle = 60 000 miles = 96 500 km
Distance travelled by fleet = 22 400 × 60 000 = 13.4 × 10^8 miles = 21.6 × 10^8 km

This figure is probably an upper bound, since non-tankers may well not travel as high an annual distance as tankers.

The ACDS figures given in Table 26.6 for that part of the tanker fleet carrying motor spirit, on relatively short journeys, imply an annual distance travelled, loaded and unloaded, of 1.64×10^8km.

Proportion of route in built-up area
The severity of a road transport accident depends in part on whether it occurs in a built-up area. The proportion of a route which passes through areas which are urban or suburban is typically of the order of 10–15%, but it varies. Detailed values for some particular routes are given in the ACDS report.

Movements of certain hazardous materials
The ACDS report given a detailed breakdown of the movements of the four materials considered, as shown in Table 23.6.

23.6.2 Road accidents

Statistics on road accidents in Britain are given in the *Annual Abstract of Statistics* by the Central Statistical Office (CSO). Further information is given in the series *Road Accidents Great Britain* by the Department of Transport (DTp).

An accident may be classified as a collision with other vehicle (COV) or a single vehicle accident (SVA). The latter may be subdivided into a collision with a stationary object (SVO) or overturning (OT).

Accident definitions
Accidents are commonly classified in the UK as personal injury (PI) accidents and damage-only (DO) accidents.

Road accident statistics derived from police records relate to personal injury accidents. The number of DO accidents generally has to be estimated from the number of PI accidents. For example, R.F.F. Dawson (1971) in a study of the cost of accidents gives the number of PI accidents in 1968 as 264 200 and estimates the number of DO accidents as 1 583 000, giving a DO/PI accident ratio of 6. Appleton states that values of the ratio given in DoT and TRRL studies are in the range 6–12. He also states that a survey by the Safety and Reliability Directorate (SRD) of a small number of local authorities found a value of the DO/PI ratio of 2–3 but the reporting was not consistent. In any event, the problem of defining what constitutes an accident is more severe for DO than for PI accidents. Moreover, an accident severe enough to endanger the integrity of a load is likely to result in some personal injury. It is convenient, therefore, to work in terms of the PI accident criterion.

The main exception to the above is fires. Fire brigade records allow the derivation of fire statistics. Major studies of fires have been made by North (1974) and McLean (1981).

The significance of the definition of an accident depends on the use to which it is to be put in the hazard assessment. Broadly speaking, the definition is important if historical data on releases are lacking, but this is less so if such statistical information is available. The reason why is that in the latter case it is possible to work with a definition of an accident which is to a degree arbitrary and to work in terms of the probability

Table 23.7 *Road transport environment in Great Britain: casualties in HGVs in 1986 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A No. of casualties

Other vehicle type	*Fatalities*	*Casualties*
HGV	24	672
LGV	–	137
Bus/coach	–	47
Car	4	622
Motorcycle	–	17
Pedal cycle	1	8
SVA (no pedestrian)	32	1045
SVA (pedestrian)	171	1184
Other	28	747
Total	260	4479

B No. of HGVs involved in injury accidents: rigid HGVs

Road type	*No. of vehicles involved*							
	Fatal accidents				*All accidents*			
	2-axle	*3-axle*	*4-axle*	*All*	*2-axle*	*3-axle*	*4-axle*	*All*
Non-BUR	239	41	50	330	3672	714	657	5082
BUR	164	32	25	221	3988	631	463	5043
All speed limits	403	73	75	551	7660	1345	1120	10125

C No. of HGVs involved in injury accidents: articulated HGVs

Road type	*No. of vehicles involved*							
	Fatal accidents				*All accidents*			
	2-axle	*3-axle*	*4-axle*	*All*	*2-axle*	*3-axle*	*4-axle*	*All*
Non-BUR	35	127	83	245	447	1444	872	2763
BUR	15	39	15	69	283	674	316	1273
All speed limits	50	166	98	314	730	2118	1188	4036

D No. of casualties by road type

Road type	*Fatalities*	*All casualties*
Non-BUR		
A roads	451	6452
B roads	34	838
Other roads	37	1095
All roads	522	8385
BUR		
A roads	205	4926
B roads	34	933
Other roads	74	2316
All roads	313	8175
All speed limits		
Motorways	73	1888
A roads	656	11378
B roads	68	1771
Other roads	111	3411
All roads	908	18448

E Proportion of casualties by road type

Road type	*Fatalities (%)*	*All casualties (%)*
Non-BURs	57.5	45.5
BURs	34.5	44.3
Motorways	8.0	10.2

F No. of occupant casualties

Occupants	*Fatalities*			*Casualties*		
	Non-BUR	*BUR*	*All*	*Non-BUR*	*BUR*	*All*
Drivers	53	8	61	1987	773	2760
Passengers	14	8	22	354	205	559
All occupants	67	16	83	2341	978	3319

of release given an accident so defined. If, on the other hand, data are not available and it is necessary to model the accident in order to determine the probability of release, the definition of what constitutes an accident becomes more significant, since it determines the accident frequency.

In the following, the UK accidents considered are injury accidents, except for fires.

Injury accidents

For vehicles generally, H.D. Johnson and Garwood (1971) found that the proportion of fatal accidents in the total of serious injury and fatal accidents for the period 1959–65 was in the range 5.1–9.2% for roads with speed restrictions of 30 or 40 mph and in the range 8.3–14.5% for other roads.

A study by the DTp (1987a) obtained for the ratio of fatal accidents to all injury accidents values in the range 0.018 : 1 to 0.025 : 1.

Some data on casualties in HGV accidents are given in Table 23.7. A study of fatal accidents involving HGVs in 1976 has been given by Riley and Bates (1980).

Grattan and Hobbs (1978) studied injuries to occupants of HGVs. In 1975 there were 3200 occupant casualties in HGVs, of which 800 were serious or fatal, the latter numbering 71. These casualties were usually the result of collision between two HGVs or between an HGV and a roadside obstacle. A 5% sample of the serious or fatal injuries was studied. All fatal injuries were associated with either massive intrusion of the cab structure or ejection of the occupant.

Hobbs, Grattan and Hobbs (1979) have examined various classifications of injury, in a study which relates the injury classifications to the length of stay in hospital.

Kletz (1986j) quotes figures given by Hills (1981) for the number of deaths from the road transport of hazardous chemicals in the UK in the period 1970–80 as 16 deaths overall, making an average of 1.23 deaths/year. From the context these are the deaths attributable to the load. Kletz also states that the average number of deaths per fatal accident is 1.5.

HGV accident frequency

In 1986 HGVs travelled 221×10^8 km and there were 13 429 accidents involving HGVs. A number of accidents involve more than one HGV. The number of HGVs involved in accidents is thus somewhat more than the number of accidents involving an HGV. The number of HGVs involved in accidents in 1986 was nearly 15 000.

Statistics on accidents involving HGVs are given Tables 23.8–23.11. Table 23.8 gives, in Section A, the number of HGVs involved in accidents; in Section B the number of accidents involving HGVs by body type and road type; and in Section C a breakdown of the road class on which the accidents occurred. Table 23.9 gives the number of HGV accidents in 1986, by the combination

Table 23.8 *Road transport environment in Great Britain: number of HGV accidents in 1986 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Number of HGVs involved in accidents

HGV type	*Road type*		
	All speed limits	*Non-BUR*[b]	BUR
Rigid	10 125	5 043	5 082
Articulated	4036	2 763	1 273
Total[a]	14 773	7 958	6 815

B Number of accidents involving HGVs

HGV type	*Road type*		
	All speed limits	*Non-BUR*[b]	BUR
Rigid	9 601	4 782	4 819
Articulated	3 828	2 621	1 207
Total	13 429	7 403	6 026

C Proportion of HGV accidents by road class

Road class	*Proportion of accidents*[c] (%)	
	Non-BUR	*BUR*
A	76	60
B	10	11
Other	14	29
Total	100	100

[a] Figures for rigid and articulated vehicles are for defined axle configurations. The total includes cases where the axle configuration was not reported.
[b] BUR, built up road. Non-BUR includes motorways.
[c] Data exclude motorways.

Table 23.9 *Road transport environment in Great Britain: number of HGV accidents in 1986 by combination of the vehicles involved (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A All accidents

Accident type	*Number*	*Proportion (%)*
Single vehicle	1994	14.8
Two vehicles	8452	63.0
Three or more vehicles	2983	22.2

B Two-vehicle and single-vehicle accidents

Accident type	*Number*	*Proportion (%)*
Single vehicle	890	8.5
Car	5271	50.4
Bus\coach	186	1.8
LGV	594	5.7
HGV	529	5.1
Motorcycle[a]	1012	9.7
Pedal cycle	723	6.9
Pedestrian	1104	10.6
Other	137	1.3
Total	10446	100.0

C Two-vehicle accidents only

Vehicle	*Proportion (%)*
Car	62.4
Bus/coach	2.2
LGV	7.0
HGV	6.3
Motorcycle[a]	12.0
Pedal cycle	8.6
Other	1.5
Total	100.0

[a] Motorcycles include combinations.

of vehicles involved. Table 23.10 gives the frequency of HGV accidents by body type, road type and road class. Table 23.11 gives the proportion of HGV accidents by junction type and by impact position.

The basic annual accident statistics for HGVs in 1986 are:

No. of accidents = 13429/year
No. of vehicles involved in accidents = 15000
Proportion of vehicles involved in accidents = 15000/435000 = 3.4%/year
Frequency of accidents = $13429/(221 \times 10^8) = 0.62 \times 10^{-6}$/km

Impact accidents
A study of the impact speed of HGVs in accidents has been made by P.A. Davies and Lees (1991a,b) based on tachograph records. Table 23.12 gives the impact speeds obtained in this study. The accidents may be regarded as a biased sample in that the accidents were sufficiently serious for the police to have an interest and may tend therefore to give an overestimate of the impact speed in injury accidents generally.

Fire accidents
An investigation of fire in road vehicles was carried out in by North (1974). Although reported in 1974, most of the data relate to 1971 and are therefore rather old. The study does, however, contain some information on certain special aspects of vehicle fires, which are given below after a consideration of the main fire statistics.

Information on the causes of fires in vehicles in 1985 has been given by the DTp (1985). In that year out of some 248000 accidents there were some 33000 fires. The causes of these fires are given in Table 23.13. It can be seen from the table that the vast majority of vehicle fires are non-crash fires.

Information from the Home Office quoted by Davies and Lees for goods vehicle fires specifically indicates that in 1986 fire brigades attended 7212 van and lorry fires. Not all of these were on a public highway.

Of the 2578 HGV fires, 2559 (99.3%) were non-crash fires and 19 (0.7%) were crash fires. No breakdown is available for non-crash fires by vehicle type, but for crash fires the breakdown is as shown in Table 23.14, Section A. The causes of the HGV non-crash fires are given in Table 23.14, Section B.

The study by North gives some information on the location of vehicle fires. His data for lorries and tankers are given in Table 23.14, Section C. They show that for HGVs some 82% of fires occur on roads. About another 10% occur in car parks, yards and garage forecourts, probably for the most part in built-up areas.

North also gives information on the number of fatalities and on the damage caused in vehicle fires, which may help to determine the severity of such fires. In 1971 there were 241 vehicle fires, of which 16 were in lorries and 10 in tankers, and in two lorry fires there was one death in each fire and in two tanker fires one death in each. In 1972 there were 289 vehicle fires, of which 19 were in lorries and 12 in tankers and in one tanker fire there were two deaths, there being no deaths in the lorry fires. Thus, for lorries, out of 35 fires two were fatal (6%) and, for tankers, out of 22 fires three were fatal (14%).

North gives information on the resultant damage in a sample of car fires in 1971. Out of 200 fires, 73 caused minor damage, 44 damaged the original compartment, 24 damaged or severely destroyed the original compartment, 15 damaged more than one compartment, 2 damaged the exterior, 40 (20%) damaged or destroyed the whole car and 2 had no recorded result.

From the above the following annual estimates can be made for HGV fires:

No. of crash fires = 19
Crash fires as a proportion of accidents = 19/13429 = 0.14%
No. of non-crash fires = 2559
Non-crash fires as a proportion of accidents = 2559/13429 = 19%

Load-threatening accidents
Investigations of accidents which might threaten the load of a large HGV transporting radioactive waste have been made by I.A. James (1986) and by Allsop *et al.* (1986).

Table 23.10 *Road transport environment in Great Britain: frequency of HGV accidents in 1986 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Accidents by road type

HGV type	*Frequency* (accidents/10^6 km)		
	All speed limits	*Non-BUR*[a]	BUR
All HGVs	0.62	0.46	1.08

B Accidents by road class (DoT, 1987b)

Road class	*Frequency* (involvements/10^6 km)	
	Non-BUR	*BUR*
A class	0.57	1.19
B class	1.15	1.21
Other	1.30	1.28
All	0.48	1.22

C Accidents by road class

HGV type	*Frequency* (accidents/10^6 km)					
	Non-BUR			*BUR*		
	A	*B*	*Other*	*A*	*B*	*Other*
All HGVs	0.66	1.32	1.51	1.05	1.08	1.13

D Accidents by body type, road class and combination of vehicles involved: car, bus/coach and motorcycle

HGV type	*Frequency* (accidents/10^6 km)								
	Car			*Motorcycle*			*Coach/bus*		
	A	*B*	*Other*	*A*	*B*	*Other*	*A*	*B*	*Other*
All HGVs	0.56	0.57	0.60	0.11	0.11	0.12	0.02	0.02	0.02

E Accidents by body type, road class and combination of vehicles involved: LGV, HGV and pedal cycle

HGV type	*Frequency* (accidents/10^6 km)								
	LGV			*HGV*			*Pedal cycle*		
	A	*B*	*Other*	*A*	*B*	*Other*	*A*	*B*	*Other*
All HGVs	0.06	0.06	0.07	0.06	0.06	0.06	0.08	0.08	0.08

F Accidents involving only a single vehicle by body type and road class: BURs

HGV type	*Frequency* (accidents/10^6 km)								
	SVA (no pedestrian)			*SVA (pedestrian)*			*Total SVA*		
	A	*B*	*Other*	*A*	*B*	*Other*	*A*	*B*	*Other*
All HGVs	0.07	0.07	0.07	0.08	0.08	0.09	0.15	0.15	0.16

G Accidents involving only a single vehicle by body type and road class: non-BURs

HGV type	*Frequency* (accidents/10^6 km)								
	SVA (no pedestrian)			*SVA (pedestrian)*			*Total SVA*		
	A	*B*	*Other*	*A*	*B*	*Other*	*A*	*B*	*Other*
All HGVs	0.04	0.08	0.09	0.05	0.10	0.12	0.09	0.18	0.21

[a] Non-BUR includes motorways.

Table 23.11 *Road transport environment in Great Britain: road position and impact position for HGV accidents (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Road position (after DpT, 1987b)

Junction type	*Proportion of accidents (%)*			
	Rigid		*Articulated*	
	Non-BUR	*BUR*	*Non-BUR*	*BUR*
Roundabout	3.4	5.5	5.0	8.9
T or staggered junction	13.7	36.0	10.0	32.9
Y junction	1.3	1.7	1.1	1.4
Crossroads	4.2	13.6	3.1	12.5
Multiple junction	0.5	1.7	0.5	2.7
Slip road	2.7	0.5	4.1	1.3
Private entrance	5.0	5.0	3.0	5.2
Other	1.0	1.6	1.0	2.1
Not at or within 20 m of junction	68.2	34.4	72.2	33.0
Total	100.0	100.0	100.0	100.0

B Impact position (after Riley and Bates, 1980)

Impact position	*Proportion of impacts (%)*				
	Car	*MC*	*LGV*	*HGV*	*All vehicles*
Front	66	41	63	53	59.4
Side	16	31	9	15	18.6
Rear	14	26	28	24	18.1
Other	4	2	0	8	3.9
Total	100	100	100	100	100.0

Table 23.12 *Road transport environment in Great Britain: impact speeds of HGVs in accidents (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Collisions involving other vehicles

Impact speed (mph)	*Non-BUR*	*BUR*	*Motorways*
0–9	1	3	0
10–19	2	4	0
20–29	1	10	2
30–39	5	12	1
40–49	9	5	2
50–60	2	2	2
>60	1	0	0
Total	21	36	7

B Single-vehicle accidents

Impact speed (mph)	*Non-BUR*	*BUR*	*Motorways*
0–9	1	0	0
10–19	3	4	0
20–29	2	11	0
30–39	2	5	1
40–49	1	6	1
50–60	0	0	2
>60	0	0	1
Total	9	26	5

Table 23.13 *Road transport environment in Great Britain: causes of fires in road vehicles 1984 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

Cause	*Number*	*Proportion (%)*
Deliberate ignition	7 434	22.0
Smokers' materials	1 165	3.4
Wiring of vehicle	8 980	26.6
Oil and petroleum in contact with hot components	8 475	25.1
Crash, collision	881	2.6
Other	4 042	12.0
Unknown	2 793	8.3
Total	33 770	100.0

The study by James is concerned with articulated, five-axled HGVs. For the determination of accident frequency he assumes that only serious accidents, i.e. those involving death or serious injury, have the potential to threaten the load. Thus James considers only accidents where the subject vehicle was an articulated HGV having a gross vehicle weight (GVW) of more than 1.5 tonne, where death or serious injury was involved, and where the accident either was a single vehicle accident or involved another HGV of GVW greater than 1.5 tonne. Table 23.15 shows his data for the number and frequency of such accidents.

Table 23.14 *Road transport environment in Great Britain: fires in HGVs 1986 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Number of crash fires

	Non-BUR	*BUR*	*All speed limits*
All HGVs	11	8	19

B Frequency of crash fires

	Frequency (fires/10^8 km)		
	Non-BUR	*BUR*	*All speed limits*
All HGVs	0.06	1.15	0.09

C Location of lorry and tanker fires (North, 1974)

Location	*Proportion of fires* (%)	
	Lorries	*Tankers*
Road or verge	71.7	67.4
Motorway	10.5	15.2
Field, open land	6.4	4.9
Cark park, yard	10.1	9.7
Garage forecourt	0.7	0.5
Garden	0.1	0.5
Other (specified)	0.5	1.6
Total	100	100

Also shown in the table are the results obtained by Allsop *et al.* They considered all injury accidents involving either four-axle or five-axle HGVs in overturning or side damage. The accident frequencies obtained by these workers are appreciably higher. For motorways and A roads their results are higher than those of James by a factor of 2–3. The factor is greater for B roads and other roads, but James' data show that the distance travelled by these large HGVs on the lower class roads is relatively small.

Chemical accidents

An account of the chemical accidents attended by the UK public fire service in 1980 has been given by McLean (1981). There were 983 special service calls in which dangerous chemicals were involved and 968 actual incidents. The incidents occurred at both fixed installations and in transport.

Table 23.16 *Road transport environment in Great Britain: nature of chemical incidents attended by the UK public fire services in 1980 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

Nature of incident	*Number of incidents*	*Proportion of incidents (%)*
Chemical overheated	9	1
Spillage	419	43
Leakage	211	22
Vapour, gas escape	80	8
Potential spillage	11	1
Fire	173	18
Explosion	10	1
Chemical found	19	2
Other	20	2
Unknown	16	2
Total	968	100

Table 23.16 gives the nature and number of these incidents. The principal chemicals involved, together with the number of incidents, were: hydrochloric acid (66), ammonia (65), LPG (42), sulphuric acid (34) and sodium hydroxide (30). There were 14 incidents involving petroleum and 10 involving ammonium nitrate. Of these incidents 132 were fires in which the presence of the chemical affected the fire fighting to a significant degree, 18 were fires in which dangerous chemicals behaved in an abnormal manner and 25 were fires at which dangerous chemicals were present and gave rise to casualties.

For all transport incidents, both road and rail, there were 419 incidents, excluding cases in which chemicals were washed ashore. Of these, 105 (25%) occurred in rural areas, 187 (45%) in urban industrial areas, 113 (27%) in urban residential areas, and the remaining 14 (3%) in unrecorded locations.

As far as concerns the road transport incidents, there were 335 incidents, of which 21 (6%) were on motorways, 120 (36%) on A class roads, 56 (17%) on B class roads, 29 (9%) on unclassified roads, 96 (29%) occurred in a parking area off the public roads, and the remaining 14 (3%) were in unrecorded locations.

In 243 (73%) of the incidents the vehicle was attended. Therefore the number of incidents in which it was unattended was as high as 92 (27%).

Table 23.15 *Road transport environment in Great Britain: number and frequency of a certain type of load-threatening accident (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

Road type	*No. of accidents*	*Distance travelled* ($\times 10^6$ miles)	*Accident frequency*[a]	
			($\times 10^{-8}$ accidents/mile)	($\times 10^{-8}$ accidents/km)
Motorway	310	3202	9.68	6.0
A class	740	3855	19.2	11.9
B class	47	172	27.0	10.4
Total	1097	7229	15.2	9.4

[a] Allsop *et al.* (1986) give an accident frequency (accidents/10^8 km) as follows: motorways, 11.5; A roads, 36.5; B roads, 114; other roads, 83.1.

In only 36 (11%) of the cases was an accident reported as the primary cause of the incident.

Background on accidents
A discussion of the UK accident statistics is given by H.D. Johnson and Garwood (1971). McBean (1982) attempts to assess the influence of road features on accident frequency and P.P. Scott (1983) that of traffic density, whilst Storie (1984) considers the effect of driver characteristics.

A study of HGV accidents was made in 1979 by Neilson, Kemp and Wilkins (1979), but the data given above are more up to date.

23.6.3 Road accidents: HGV/HMs

Accident frequency for HGV/HMs
HGVs carrying hazardous materials have a higher standard of design and operation, although the extent of this is variable. It may therefore be expected that the accident rate would be less. Information obtained by P.A. Davies and Lees (1992) for munitions vehicles indicates a reduction factor of about 0.1–0.33. For HGV/HMs it seems doubtful whether such a large reduction is appropriate. The estimate used by Davies and Lees is 0.8.

M. Griffiths and Linklater (1984) found that the proportion of HGV/HMs suffering an accident was the same as for HGVs generally. Although a lower accident rate per unit distance travelled is assumed here for HGV/HMs, these vehicles travel a greater distance per year, and the net effect is to give them an annual accident rate comparable with or rather greater than that of other vehicles.

Taking the estimate

Ratio of HGV/HM to HGV accident rates = 0.8

then for HGV/HM accidents

Frequency of accidents = $0.8 \times 0.62 \times 10^{-6}$/km = 0.50×10^{-6}/km
No. of accidents = $0.50 \times 10^{-6} \times 21.6 \times 10^{8}$ = 1080 accidents/year
No. of vehicles involved in accidents = (15 000/13 429) × 1080 = 1206
Proportion of vehicles involved in accidents = 1206/22 400 = 5.4%/year

For Ministry of Defence munitions vehicles (MVs), taking the estimate

Ratio of MV to HGV accident rates = 0.2

then

Frequency of accidents = 0.12×10^{-6}/km

Release frequency and probability for HGV/HMs
An estimate of the frequency and probability of release given an accident can be made from the data given by Maclean. From his data:

No. of releases due to traffic accidents = 36

then

Frequency of release = $36/(21.6 \times 10^{8})$
= 0.017×10^{-6} releases/km
= 0.027×10^{-6} releases/mile

Probability of release given traffic accident = 36/1080
= 0.033
= 3.3%

These estimates are based on attendance by a fire brigade and should be regarded as lower limits.

These results may be compared with the US figures. Tables 23.18–23.20 (see below) give for the USA data on the probability of release and on the frequency of release per unit distance travelled. Again in both cases a distinction has to be made between releases occuring as a direct result of a traffic accident and releases due to other causes. The data given in Table 23.19 are particularly relevant in this regard.

Fatal accidents for HGV/HMs

Ratio of fatal accidents to injury accidents = 0.022
No. of fatal accidents = 0.022 × 1206 = 26.5/year
No. of fatalities per fatal accident = 1.5
No of fatalities from accidents = 1.5 × 26.5 = 39.8, say 40

About one death per year is attributable to the load and the rest are due to traffic accidents.

23.6.4 Collision modelling: impact speed

The attempt to estimate the frequency of a particular type of event arising from an HGV collision will depend both on the probability of the event given a collision with a particular effective impact velocity, and on the frequency of a collision of sufficient severity with this impact velocity.

The effective impact velocity will depend on the closing, or impact, speed. For a single vehicle accident all that is required is the impact speed of a single HGV. Data which may be used to construct a probability density function for HGV closing speeds in accidents are given in Table 23.12. For an accident involving two vehicles it is necessary to combine the probability density functions of the two vehicles. In such cases the probability density function for the HGV impact speed may be used for both vehicles.

An approach to the determination of the probability of a given combined impact speed in a head-on collision of two HGVs is as follows. Given that there is available a distribution of HGV impact speeds such as that shown in Table 23.12, the distribution of the impact speeds of an HGV–HGV head-on collision and the probability that the speed lies within a certain range may be obtained as follows. Consider a normal distribution of HGV impact speeds $f(x)$ on built-up roads, where x is the impact speed, with a mean $\bar{x}$ and standard deviation σ. Then for the distribution $f(x_c)$ of the combined (i.e. summed) impact speeds

$$\bar{x}_c = 2\bar{x} \qquad [23.6.1]$$

$$\sigma_c^2 = 2\sigma^2 \qquad [23.6.2]$$

$$\sigma_c = 2^{\frac{1}{2}}\sigma \qquad [23.6.3]$$

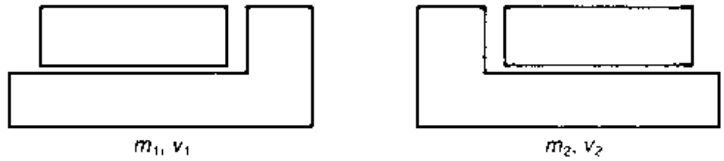


Figure 23.4 *Vehicle collision model*

The probability P that the combined impact speed x_c lies between x_{c1} and x_{c2} is then

$$P(x_{c1} < x_c < x_{c2}) = P\{[(x_{c1} - \bar{x}_c)/\sigma_c] < x_c < [(x_{c2} - \bar{x}_c)/\sigma_c]\} \quad [23.6.4]$$

$$= P(a < x_c < b) \quad [23.6.5]$$

$$= I(b) - I(a) \quad [23.6.6]$$

$$= P \quad [23.6.7]$$

where subscripts 1 and 2 denote bounding values of speed. Values of *I(a)* and *I(b)* can be obtained from standard tables of the normal distribution.

As an illustration, consider the following example:

$\bar{x} = 30.6$ mph

$\sigma = 12.2$ mph

$\bar{x}_c = 2 \times 30.6 = 61.2$

$\sigma_c = 2^{\frac{1}{2}} \times 12.2 = 17.3$ mph

The probability that the collision speed is between 110 and 130 mph is then

$P[(110 - 61.2)/17.3 < x_c < (130 - 61.2)/17.3]$

$= P(2.28 < x_c < 3.98) = I(3.98) - I(2.82)$

$= 0.9999 - 0.9976 = 2.3 \times 10^{-3}$

This method provides a simple and rapid estimate of the probability of the combined collision speed, given a collision. The results are, however, only as good as the quality of fit of the distribution used. Specifically, the method utilizes the tail of the distribution. The fitting and use of tails is a common problem in the use of distributions. In some cases it may be preferable to use alternative methods such as Monto Carlo simulation using the actual histogram data for collision speeds.

23.6.5 Collision modelling: impact consequences

There are several collision scenarios which may be relevant to the conveyance by road of hazardous materials. Loss of containment of hazardous liquids in bulk transport is the prime problem, but explosion of loads sensitive to shock may also be of concern.

The modelling of vehicle collision is discussed in *Handbook of Road Safety Research* (Grime, 1987).

For loss of containment of a hazardous liquid there will be critical combinations of the impact velocities at which penetration of the tank occurs. For a frontal collision of two vehicles, by conservation of energy

$$\tfrac{1}{2}(m_1 v_1^2 + m_2 v_2^2) = \tfrac{1}{2}(m_1 + m_2)v^2 + E \quad [23.6.8]$$

and by conservation of momentum

$$v = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2} \quad [23.6.9]$$

where E is the energy absorbed in the collision, m_1 is the mass of the first vehicle, m_2 is the mass of the second vehicle, v is the residual velocity of the two vehicles after the collision, and v_1 is the initial velocity of the first vehicle and v_2 is that of the second vehicle. The mass of each vehicle is defined here as that of the vehicle plus its load which is assumed to be restrained.

From Equations 23.6.8

$$E = \tfrac{1}{2}[m_1 v_1^2 + m_2 v_2^2 - (m_1 + m_2)v^2] \quad [23.6.10]$$

Equation 23.6.10 may be used to determine the critical combination of velocities v_1 and v_2 which give the critical energy absorption E_{cr} for rupture of the containment. The latter factor is obtained from mechanical considerations for the particular tanker.

An early example of such an approach was the investigation by Westbrook (1974) of the comparative risks of chlorine transport by road, rail and pipeline. The study included a road tanker collision analysis to determine the probability of puncture given a crash.

A series of collision analysis studies for HGVs for US conditions is available in Gardner and Moffatt (1982).

For the explosion of a shock sensitive load there will be some critical impact velocity of the load at which explosion occurs. For a frontal collision of a vehicle carrying such a load unrestrained with another vehicle as shown in Figure 23.4 by conservation of momentum the residual velocity v of the two vehicles is given by Equation 23.6.9. This velocity may be positive or negative. Then the impact velocity v_l of the load is

$$v_l = v_1 - v \quad [23.6.11]$$

Equation 23.6.11 may be used to determine the critical combination of velocities v_1 and v_2 which give the critical impact velocity v_{lcr} for the load.

The treatment of ship collision, described below, presents close parallels to road collision analysis of the type just described.

23.6.6 Releases

Moving on to accidents resulting in releases, the ACDS report considers two categories of accident: (1) the puncture of a tank wagon in an accident and (2) failure or maloperation of the tanker equipment.

It considers the four study materials in turn. For motor spirit

Table 23.17 *Road transport environment in Great Britain: number of spills of motor spirit August 1980–August 1985*[a] *(Advisory Committee on Dangerous Substances, 1991) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

Initiating event	*Spill mechanism*	*Spill size* (kg)			
		< 15	*15–150*	*150–1500*	*> 1500*
Rollover	Puncture			1	4
	Equipment		1	1	3
	Not specified		2		
Collision	Puncture		1		2
	Equipment		1	1	
	Not specified		1		
Body material and equipment failure	Top hatch		1		
	Pipework	1	2		
	Material crack	1	2		
Total		2	11	3	9

[a] The period considered is given in Tables 4 and 5 of the report as starting in August 1981, but in Table 6 as starting in 1980. The latter fits the estimate given for motor spirit tankers on p. 235, para 32, of the report for the puncture frequency $= 1.9 \times 10^{-8}$ per loaded tanker km and is adopted here.

Distance travelled $= 82 \times 10^6$ tanker-km/year

This figure, and the others quoted in this section, refer to loaded journeys only.

The number of spills of motor spirit in the 5 year period ending in August 1985 is shown in Table 23.17. The spills are classed as nuisance (< 15 kg), small (15–150 kg), medium (150–1500 kg) and large (> 1500 kg).

For spills of motor spirit due to punctures:

Frequency of spills due to punctures of motor spirit tankers $= \frac{8}{5} \times \frac{1}{82 \times 10^6}$

$= 1.9 \times 10^{-8}$/tanker-km

The frequency of medium spills due to punctures is 1.4×10^{-8}/tanker-km and that of large spills 0.24×10^{-8}/tanker-km.

There were no punctures of LPG, ammonia or chlorine tankers in the observation period, if two incidents involving the transport of ammonia and LPG in improperly designed tankers are disregarded. However, from an ICI analysis of US data showing 12 LPG puncture incidents, the frequency of spills due to puncture of US LPG tankers was estimated as 8.1×10^{-9}/tanker-mile. Then, allowing for the higher frequency of level crossing incidents in the USA and for differences in tanker design, the frequency of spills due to puncture of UK LPG tankers was obtained as 4.8×10^{-10}/tanker-km. A similar value was assumed for ammonia, whilst for chlorine the frequency was estimated as 0.8×10^{-10}/tanker-km.

For motor spirit spills due to equipment failures, the frequency of small spills, including those with causes not specified, is 1.9×10^{-6}/journey, that of medium spills 3.0×10^{-6}/journey and that of large spills 4.5×10^{-6}/journey.

With regard to spill size, the average size of spill in six puncture incidents was 4015 kg and that in three equipment failure incidents was 3640 kg.

For the other three substances, the frequency of leaks due to equipment failure was obtained from fault trees which are given in the report. The results for all spills other than nuisance spills were as follows:

	Frequency of spill (spills/journey)
LPG	5.2×10^{-9}
Ammonia	7×10^{-9}
Chlorine	3.6×10^{-9}

23.6.7 Release ignition

For the probability of ignition of a spill of flammable material, the ACDS report states that none of the 25 spills considered ignited. It disregards the two nuisance spills (< 15 kg) and obtains from the remaining unignited spills an expected value of 0.7 ignitions in 23 spills, or an ignition probability of 0.033.

This value is lower than that adopted for rail spills, as described below. This appears surprising, since other vehicles are potential sources of ignition. The report gives as possible reasons the good drainage of roadways and the emergency action taken by tanker drivers. It also quotes expert judgement that a probability of ignition of one in thirty is about right.

23.6.8 Fires

The other main event which may give rise to an incident is fire. The frequency of fires on HGVs was considered in Section 23.6.2. With regard to fire, for HGVs generally non-crash fires are much more frequent than crash fires. The Australian work indicates, not surprisingly, that this is less so for road tankers carrying flammable materials. Nevertheless, the figures suggest that even for such tankers non-crash fires may be more significant.

23.6.9 Lorry stopover point incidents

The ACDS report also considers the hazard at lorry stopover points. These may vary from overnight lorry parks to points where the stopover is less than 1 hour.

COP 11 states that when a vehicle is not being driven it should be parked in a safe place or supervised at all times by the driver or other competent person. It recommends that for periods of parking in excess of 1 hour, or for overnight parking, use should be made of a lorry park or some other place where the public do not have access.

The report states that UK records contain no puncture incident in a lorry stopover point. The authors therefore attempt to derive an estimate by adapting the *en route* puncture frequency data described above. These data, which are expressed as a frequency of puncture per tanker-km, are converted to a frequency of puncture per tanker-hour using a notional average speed of 60 mph. The data are corrected to allow for the low speed of vehicles in lorry stopovers by applying for motor spirit tankers and LPG tankers correction factors of 0.1 and 0.01, respectively. The frequency of punctures per journey is then obtained using appropriate values for the length of a stopover, taken as typically half an hour, and for the number of stopovers, taken as averaging 1.5 per journey.

For LPG the *en-route* frequency of puncture of a tanker is 4.8×10^{-10}/tanker-km and there are 63 667 journeys/year. Then, following the approach just described

Frequency of puncture of tanker $= 0.01 \times 60 \times 4.8 \times 10^{-10}$/tanker-km
$= 2.88 \times 10^{-10}$/tanker-h

With 1.5 stopovers/journey and a stay of 0.5 h/stopover

Frequency of puncture of tanker $= 1.5 \times 0.5 \times 2.88 \times 10^{-10}$
$= 2.2 \times 10^{-10}$/journey
$= 63\,667 \times 2.2 \times 10^{-10}$
$= 1.4 \times 10^{-5}$/year

The frequency of leaks due to equipment failure was obtained from fault trees, one of which, that for LPG, is given in the report.

Using this methodology the results obtained for all four study substances in lorry stopover points are as follows:

	Frequency of puncture (punctures/journey)	*Frequency of spills due to equipment failure* (failures/h)
Motor spirit	2.9×10^{-9}	–
LPG	2.2×10^{-10}	2.6×10^{-9}
Ammonia	1.4×10^{-10}	3.9×10^{-9}
Chlorine	1.4×10^{-11}	1.3×10^{-9}

No evaluation of equipment failure frequency was made for motor spirit, since the consequences were judged to be minor.

23.6.10 Exposed population

The population exposed in a road transport accident are the *en-route* population and the other road users together with the emergency services. Meaningful assessment of the societal risk from road transport requires the use of a reasonably refined population exposure model. The models used in the ACDS report are described in Appendix 17.

Population density and other characteristics

A study of the density and other characteristics of the population which might be exposed to hazardous materials has been made by Petts, Withers and Lees (1987). The information given includes data for the UK on population densities, both by day and by night, on the proportions of persons indoors and outdoors, and on the proportion of the population which may be considered particularly vulnerable.

There have also been specialist studies of the population density along routes taken in the transport of hazardous materials. These include the TRIP program referred to in the Second *Canvey Report* (HSE, 1981a) and the study by Canadine and Purdy (1989) already mentioned.

High density targets

Of particular interest is the probability that any incident will occur at a location where large numbers of people are exposed. An estimate of this probability for built-up areas may be made from V-2 rocket incidents. The distribution of the rockets which fell on London was effectively random. Analysis of the 517 V-2 incidents in London gives 8.9% which caused $\geq$10 deaths and 1.4% which caused $\geq$33 deaths.

Emergency services

In addition to the population who are normally in the area, emergency services personnel who attend the accident are also at risk. It is not uncommon in an incident involving the road transport of hazardous materials that a significant proportion of the casualties include such personnel.

A typical road accident involving injury and fire would probably be attended by one police patrol car (2 persons), one fire tender (4–5 persons) and one ambulance (2–3 persons). If the incident is considered serious and time permits, additional fire tenders may attend.

23.6.11 Emergency services

Attendance times

In assessing the consequences of an incident, the time for the fire services to attend may be important. In accordance with Home Office guidance, fire brigades classify areas into different categories of risk. For each category there is a specified minimum number of pumps (i.e. fire engines) which are required to attend the scene and a maximum time for their arrival. A vehicle fire is normally attended by one fire engine. Information from the London Fire Brigade obtained by P.A. Davies and Lees (1992) indicates that a vehicle fire is normally attended by one fire engine and that for the type of area through which, for example, road transport of explosives takes place, the maximum attendance time is 20 minutes.

The mean attendance time is between 10 and 15 minutes.

23.6.12 North American environment

There have been a number of studies in North America on the transport of hazardous materials. Several of the more recent studies are considered here.

A review of accidents involving, and releases from, vehicles carrying hazardous materials has been given by Glickman (1988). The data are based on the reporting system of the Department of Transportation, Office of Hazardous Materials Transportation. The basic data consist of the distance travelled by trucks carrying hazardous materials and the number of accidents involving a spillage.

The reporting system requires the recording of any unintentional release occurring during loading/unloading, transportation, or temporary storage. The author equates such releases to spillages. Spillages are treated as significant if they involve more than 5 US gallons or 40 lb of material. From these reporting requirements, from the data given by Maclean above and from other data given below, it would seem that most of these spillages do not in fact occur due to road traffic accidents on the public highway.

Some data from the study are shown in Table 23.18. The frequency of spillages is obtained by simply dividing the number of spillages by the distance travelled by the vehicles.

There are several points of interest in these data. One is the rather high ratio of the distance travelled by vehicles other than tank trucks to that travelled by tank trucks. Another is the rather lower ratio of the number of significant spillages for vehicles other than tank trucks to the number for tank trucks. Also of interest is the striking difference in the frequencies of spillage between private trucks and trucks for hire.

The overall frequency of significant spillages is

$$\text{Frequency of significant spillages} = 1667/(16\,220 \times 10^6) = 0.10 \times 10^{-6} \text{ spillages/vehicle-mile} = 0.062 \times 10^{-6} \text{ spillages/vehicle-km}$$

Harwood, Russell and Viner (1989) have collated information on hazardous material (HAZMAT) accidents. This information was obtained from the Department of Transportation's Research and Special Programs Administration (RSPA) Hazardous Materials Incident Reporting (HMIR) System data base. The system is based solely on self-reporting by carriers. No minimum release quantity or damage level is specified and, technically, any release, however small, is reportable. The requirements apply, however, only to interstate transport, and carriers engaged solely in intrastate transport are not required to report HAZMAT incidents under this scheme.

Data were analysed for the period 1981–85. During this time there were 28 433 HAZMAT incidents reported. Some data on these incidents are given in Table 23.19. As the table shows, the proportion of HAZMAT incidents due to traffic was 11%. However, the proportion of severe incidents due to traffic lay between 35% and 68%, depending on the definition of severity. The authors give one definition of a severe incident as one involving injury or death, a fire or explosion or more than US$50 000 dollars worth of damage.

The authors also give information from another database, the Motor Carrier Accident Report maintained by the FHWA Bureau of Motor Carrier Safety (BMCS), now renamed the Office of Motor Carriers. This database gives information on trucks involved in accidents, including whether the truck was carrying hazardous materials and whether a release occurred. The reporting

Table 23.18 *Road transport environment in North America: the distance travelled and the number and frequency of spillages for US trucks carrying hazardous materials in 1982 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Distance travelled

Type of vehicle	*Distance travelled* (10^6 vehicle miles)
Trucks	
Private	6 416
For hire	9 804
Total	16 220
of which	
Tank trucks	
Private	4 121
For hire	307
Total	4 228

B Number of spillages

Type of vehicle	*No. of spillages*	
	Total	*Significant*
Trucks		
Private	357	233
For hire	5314	1434
Total	5671	1667
of which		
Tank trucks		
Private	248	178
For hire	936	692
Total	1184	870

C Frequency of spillages

Type of vehicle	*Frequency of spillages* (spillages/10^6 vehicle miles)	
	Total	*Significant*
Trucks		
Private	0.0556	0.0363
For hire	0.542	0.146
of which		
Tank trucks		
Private	0.0602	0.0432
For hire	3.049	2.254

Table 23.19 *Road transport environment in North America: hazardous material incident data from the US Department of Transportation RPSA database for 1981–85 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Location of incidents

Location	*Proportion (%)*	*Number*
On public highway	48	13 547
Off public highway	39	*c.* 11 089
Unknown	13	*c.* 3 797
Total	100	28 433

B Failure involved in incidents on public highway

Failure type	*Number*	*Proportion (%)*
Traffic accident	1 427	10.8
Body or tank failure	2 741	20.2
Valve or fitting failure	3 289	24.3
Cargo shifting	4 945	36.5
Fumes or venting	15	0.1
Other	1 100	8.1
Total	13 547	100.0

C Hazardous materials involved in incidents on public highway

Material	*All incidents (%)*	*Traffic incidents (%)*
Flammable liquids	46	71
Toxic liquids	5	
Corrosive liquids	40	13

D Consequences of incidents on public highway

Count	*Number of incidents*		
	Traffic incidents	*Other incidents*	*All incidents*
No. of incidents	1 457	12 090	13 547
No. of deaths	50	4	54
No. of injuries	115	358	473

Table 23.20 *Road transport environment in North America: data on HAZMAT trucks involved in accidents from the US Department of Transportation BMCS database for 1984–85 (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Truck accidents

Truck type	*Number*
Non-HAZMAT trucks	71 164
HAZMAT trucks	3 703
of which	
No release	3 183
Release	530

B Cargoes of HAZMAT trucks in accidents

Cargo	*Number of accidents*		
	No release	*Release*	*Total*
General freight	680	61	741
Gases in bulk	238	21	259
Solids in bulk	28	12	40
Liquids in bulk	1486	345	1831
Explosives	63	7	70
Empty	210	10	220
Other	467	62	529

C Consequences of HAZMAT truck accidents

Count	*Number of accidents*		
	No release	*Release*	*Total*
No. of incidents	3183	520	3703
No. of deaths	273	53	326
No. of injuries	2514	441	2955

system applies, however, only to interstate carriers. Data from this source are given in Table 23.20.

An analysis of accident rates in three states (California, Illinois and Michigan) and of release probabilities overall in the USA has been given in a study by Harwood, Viner and Russell (1990), which follows on from the authors' earlier work (Harwood and Russell, 1989; Harwood, Russell and Viner, 1989). The data were obtained from the accident reporting systems of these states. Table 23.21 gives data on release frequencies and probabilities.

The accident frequencies differ appreciably between the different classes of highway. They also apparently differ appreciably between states. The probabilities of release given an accident, however, are relatively similar for rural highways as a group and for urban highways as a group.

An analysis of incidents in Canada in which there were releases of gasoline or LPG has been made by Steward and van Aerde (1990a). The incidents were those reported under the regulatory system as dangerous occurrences in the period 1986 to August 1987 (1.7 years). Thus not all accidents were reported and the data are therefore not comparable with those reported under the US HAZMAT scheme.

There were 41 incidents involving gasoline. A proportion of these may not have been transport incidents. The proportion known to be transport incidents was 81%, leaving between 0% and 19% which may not have been. Table 23.22 gives the number of incidents by type of release.

The three major types of incident were collision, collision/overturn and overturn. The proportion of lading released in these cases was 30–40%. For fires, the release was large (98%) except in one case where it was very small (3%). Of these three types of incident, overturns caused most container damage. The authors suggest that

Table 23.21 *Road transport environment in North America: probability and frequency of release of material in truck accidents in the USA (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Probability of release by accident type: single vehicle accidents

Accident type	*Probability of release*
Non-collision accidents	
Run off road	0.331
Overturn	0.375
Other	0.169
Collisions with:	
Fixed object	0.012
Parked vehicle	0.031
Train	0.455
Non-motorist	0.015
Other object	0.059

B Probability of release by accident type: multiple vehicle accidents

Accident type	*Probability of release*
Collision with:	
Passenger car	0.035
Truck	0.094
Other vehicle	0.037

C Probability and frequency of release by road type

Road type	*Probability of release*	*Frequency of release (release/10^6 vehicle-miles)*
Rural		
Two-lane	0.086	0.19
Multi-lane (undivided)	0.081	0.36
Multi-lane (divided)	0.082	0.18
Freeway	0.090	0.06
Urban		
Two-lane	0.069	0.60
Multi-lane (undivided)	0.055	0.77
Multi-lane (divided)	0.062	0.77
One-way street	0.056	0.54
Freeway	0.062	0.14

in collision accidents a large proportion of the energy is dissipated in other parts of the vehicle.

There were four evacuations of the public in the 41 incidents.

A similar analysis is given for the LPG incidents, but there were only nine of these.

Further more general data are given in the review of transportation of hazardous materials in Ontario by Gorys (1990).

Griffiths and Linklater (1984) have reported a study performed in 1980 of some 42 accidents involving road tankers transporting flammable materials in New South Wales (NSW). In 1979 in NSW there were some 3000 road tankers carrying flammable loads and some 100 pressurized tankers. The annual crash rate was 2.5%, which was the same as for all vehicles.

There were 42 accidents investigated, 11 involving non-articulated vehicles and 31 involving articulated vehicles. There were 18 rollovers, 5 for the non-articulated vehicles and 13 for the articulated vehicles.

In 24 cases there was no leakage of the bulk load but in three of these there was leakage of the prime mover fuel tanks. In 10 of the rollover cases there was substantial leakage. In two of the non-rollover cases the tank was punctured and burned out. Of the other non-rollover cases, one involved the loss of 'a lot' of product from a fractured pipe fitting, one a loss from a discharge pipe and two loss from vents.

The authors state that fire occurred in 5% of cases. This would seem to cover the two cases of burnout just mentioned and to imply that none of the other cases involved a fire.

The authors obtained data on the various factors which influenced the accident under the headings: mechanical, environmental, behavioural and general.

Factors causing rollover included high centre of gravity, 'soft' roll stiffness and sloshing of the liquid. None of the tankers appeared to have side baffles.

From these data the following estimates may be made for crash fires:

No. of crash fires = 2
Crash fires as proportion of accidents = 2/42 = 4.8%

23.6.13 Individuality of accidents

It is easy in a preoccupation with incident statistics to lose sight of the individual nature of some of the accidents which have occurred involving the road transport of hazardous materials. Mention has already been made of the chlorine tanker crash with a lorry travelling down hill at 60 mph. Other incidents with rather unusual features include the San Carlos campsite disaster (Appendix 16), which may not have been initiated by either crash or fire and which involved a vulnerable target, and the explosion of an explosives lorry at Peterborough (Case History A125), which involved a fire rather than a crash and occurred off the road in a company yard.

Moreover, enough has been said to indicate that, even where historical data do exist, the data may or may not be directly applicable. A case in point is the provision of side protection on tankers. This is provided on the ICI chlorine vehicles but not on the Australian road tankers described. In such cases it may be appropriate to modify any historical data to take account of the difference between the conditions to which those data apply and the conditions of the problem in hand. Again this may involve modelling and the use of data appropriate to that.

23.7 Rail Transport

23.7.1 Regulatory controls and codes

The international transport of dangerous goods by rail is the subject of the Convention Concerning International Carriage by Rail (COTIF) and is governed by the *Regulations Concerning the International Carriage of*

Table 23.22 *Road transport environment in North America: tanker accidents involving release of gasoline in Canada (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

Accident type	*No. of releases*						*Proportion (%)*
	Spill	*Leak*	*Spill/fire*	*Fire*	*Other*	*Total*	
Collision	2			1		3	7
Collision/overturn	5		1			6	15
Overturn	19	1			1[a]	21	51
Brake failure	2					2	5
Puncture	2	1				3	7
Fitting/hose failure		1		1		2	5
Fire				2[b]		2	5
Military exercise	1					1	2
Bridge collapse	1					1	2
Total	32	3	1	4	1	41	

[a] Environmental contamination.
[b] One of these is classified as a spill/fire.

Dangerous Goods by Rail (RID) (DTp, 1993b), as described in Section 23.2.

In addition, the International Union of Railways (IUR) issues information of an obligatory or recommended nature.

In the UK British Rail (BR) has a number of internal regulations. There is no requirement on BR to accept dangerous goods for carriage. It has published the document *List of Dangerous Goods and Conditions of Acceptance* (LDG) (BR 22426) which lists the dangerous substances that it is prepared to accept and the conditions of such acceptance. The list is based on the United Nations (UN) classification. It incorporates relevant statutory requirements such as those for radioactive materials. The conditions cover maximum quantities, forms of packaging, labelling, documentation, etc., and conform as far as possible with UN recommendations. The Railways Act 1845 requires the consignor to give written indication of goods which are dangerous, and the Railways Act 1921 requires it to comply with the rules laid down by BR.

In addition to BR's general regulations, rules and procedures, for dangerous goods there are specific instructions to staff given in *The Working Manual for Rail Staff*, Part 3, *Handling and Carriage of Dangerous Goods* (BR 30054/3), commonly known as the 'Pink Pages'. This deals with the definition of dangerous goods and gives procedures for acceptance, marking, loading, unloading, marshalling and movement, and for incidents and fires.

In the USA, rail transport of hazardous materials is regulated by the Department of Transportation (DOT). The DOT Hazardous Materials Regulations (49 CFR Pt 179) apply to carriage by rail. The Association of American Railroads (AAR) complements the work of the DOT by setting standards.

23.7.2 Hazard scenarios

The hazard scenarios for rail transport of hazardous materials do not differ greatly from those for road described in Section 23.5. Thus pool fires, torch fires, vapour cloud fires and explosions, and toxic releases may all occur in a broadly similar manner, as well as physical explosions and condensed phase explosions.

There are, however, a number of differences. One is that the energy in a train collision is much greater than that associated with a vehicle collision on a road. Another is that a train typically contains a number of tank wagons and these may be vulnerable to the initiating incident A particular instance of this is that torch fires in which the flame from one tank wagon plays on another are much more significant. The rail environment also differs in respect of the population exposed to the event and of the access for the emergency services.

23.7.3 Rail tank wagon design

The RID gives requirements for the design of rail tank wagons which parallel those in the ADR for road tankers. For more hazardous materials it is good practice to provide a strongly protected filling connection cover and buffer override protection. Rail tank wagons for LPG are shown in Plate 31.

Information on rail tank cars in the USA is given by Fitch (1986) in the *NFPA Handbook*. American rail tank cars are built to standards for freight cars generally and in addition must comply with the DOT Hazardous Materials Regulations and the *Specifications for Tank Cars* of the Association of American Railroads (AAR). There are four main types of tank car:

(1) non-pressure tank cars;
(2) pressure tank cars;
(3) cryogenic liquid tank cars;
(4) other –
    (a) high pressure service tank cars,
    (b) multi-unit tank cars.

Non-pressure tank cars have tank test pressures of 100 psi (6.89 bar) and pressure tank cars have test pressures of 100–600 psi (6.89–41.4 bar). Both types have capacities ranging from 4000 to 45 000 USgal (145–170 m^3). Cryogenic liquid tank cars carry liquids at −130 to −423°F (−90 to −253°C). The insulation is designed to protect the cargo for a 30 day period.

Multiunit tank cars, or ton containers, carry demountable tanks which can be taken off the car for filling and emptying.

About 90% of the tank cars are constructed in carbon steel and most of the rest in aluminium. The regulations specify the following thicknesses of plate for the construction of tank cars: for non-pressure tanks, $\frac{7}{16}$ in. (11.1 mm) steel or $\frac{1}{2}$ in. (12.7 mm) aluminium, and for pressure tanks, $\frac{9}{16}$ in. (14.3 mm) steel and $\frac{5}{8}$ in. (15.9 mm) aluminium.

Tank cars may be provided with thermal insulation. The principal materials used are fibreglass and polyurethane foam. For cryogenic tanks perlite is used. Some tanks are lined and some have heating coils.

The DOT has promoted a programme of protective measures to lessen the risk of tank rupture by overheating or puncture. These are:

(1) Thermal protection;
(2) Shelf couplers;
(3) Head shields.

The thermal protection is designed to protect the tank against a pool fire for 100 minutes or against a torch fire for 30 minutes. The shelf couplers are of a design which is less likely to disengage in a derailment. The head shields protect the lower part of the tank heads against puncture.

23.7.4 Rail system operation

The development of British practice in the movement of bulk chemicals by rail has been described by Sanderson (1981). The older method was to move small numbers of wagons through a series of marshalling yards; the newer method is to make up complete trainloads, or block trains, running between two points, so that rail transport becomes an integral part of the production line linking two works.

BR controls the movement of freight through the Total Operations Processing System (TOPS) computer system. This system makes it possible to keep track both of the movement of each individual wagon and of its position on the train. The system is particularly valuable in an emergency.

23.8 Rail Transport Environment

The basic sources of information on the rail transport environment in the UK are the Department of Transport and British Rail.

The *Transport Statistics Great Britain* 1976–86 (DTp, 1987b) and *Rail Safety—Report on the Safety Record of the Railways in Great Britain 1986* (DTp, 1987a) provide certain basic information. There are also available an appreciable number of accident reports.

Studies of the UK rail transport environment are given in the ACDS *Transport Hazards Report* (ACDS, 1991) and by P.A. Davies (1990). As already stated, the former considered four hazardous materials (motor spirit, LPG, chlorine and ammonia, and also explosives) whilst the latter was concerned with explosives, particularly munitions. Essentially these studies utilize two basic categories of information: (1) rail movements, and (2) incident records.

Table 23.23 *Rail transport environment in Great Britain: tank wagon capacities and movements for four hazardous materials (after ACDS, 1991) (Courtesy of Elsevier Science Publishers)*

A Tank wagon capacities

Substance	*Tank capacity* (te) *2-axle*	*Bogies*
Motor spirit	32	75
LPG	20	40
Ammonia	–	53
Chlorine	29	–

B Tank wagon movements

	Motor spirit	*LPG*	*Ammonia*	*Chlorine*
Total movements (wagon-km/year)	10 199 095	1 390 590	1 348 080	313 668
Total wagon journeys (wagon-journey/year)	55 814	4 334	4 500	2 342

23.8.1 Rail network and rolling stock

BR operates a rail network with 22 423 km of running line and 3601 km of sidings. There are some 70 marshalling yards.

In 1986 the distance travelled by freight trains was 54×10^6 km. In the year 1985–86 the distance travelled by loaded tank wagons containing both hazardous and non-hazardous chemical and petroleum products was 47.4×10^6 tank-wagon-km.

The ACDS report gives a detailed breakdown of the movements of the four materials considered, as shown in Table 23.23.

23.8.2 Rail accidents

Information on accidents involving freight trains generally is given in the study by Davies. The three main types of accident considered are collisions, derailments and fires.

The ACDS study deals mainly with accidents resulting in releases and with the ignition of releases of flammable materials.

From a study of general rail accident statistics, Davies gives the following breakdown of freight train accidents in 1986:

Type of accident	*No.*	*Proportion* (%)
Collision	113	35
Derailment	158	49
Fire	53	16
Total	324	100

He also made a study of some 187 accident reports, of which 38 were for freight train accidents (FTAs). This is

referred to as the FTA study. In this study he obtained the following breakdown of freight train accidents:

Type of accident	*No.*	*Proportion* (%)
Collision	26	68
Derailment	8	21
Fire	1	3
Other	3	8
Total	38	100

23.8.3 Collisions

In general, freight train collision accidents are more severe than derailments. For collisions in 1986, Davies gives:

Type of collision	*No.*	*Proportion* (%)
FT vs FT	8	7
FT vs PT	1	1
FT vs ECS	10	9
Buffer stop	55	49
Level crossing	6	5
Miscellaneous obstacles	22	19
Animals	9	8
Other	2	2
Total	113	100

where ECS denotes empty coaching stock, FT denotes freight train and PT denotes passenger train. The most severe collisions are with rolling stock. From the data just given there were 19 such incidents (17%) which break down to give:

Type of collision with rolling stock	*No.*	*Proportion* (%)
FT vs FT	8	42
FT vs PT	1	5
FT vs ECS	10	53

From the FTA study he found that some 70% of collisions with rolling stock were head-on or front/rear collisions and obtained for these the following breakdown:

Type of collision with rolling stock	*Proportion* (%)
Head on	40
Front on rear	40
Rear by front	20

The other 30% of collisions with rolling stock were side impacts or glancing blows.

The most frequent type of collision was with buffer stops but the speed at which these collisions occurred was generally 10 mph or below. This type of collision was considered sufficiently minor that in 1987 the practice of recording it was discontinued. It is worth noting, however, that a major disaster due to a collision of this type on a passenger train on the London Underground occurred at Moorgate station in 1975.

The number of collisions at level crossings involving freight trains was small, but for all trains the following breakdown was obtained:

Type of collision	*No.*	*Proportion* (%)
Train on car or van	18	78
Car or van on train	5	22
Total	23	100

The closing speeds at which collision accidents occurred are not known, but from an analysis of the freight train accidents in the FTA survey, P.A. Davies and Lees (1991a) obtained the estimates shown in Table 23.24, Section A.

Table 23.24 *Rail transport environment in Great Britain: accident speeds of freight trains (P.A. Davies and Lees, 1992) (Courtesy of Elsevier Science Publishers)*

A Freight train closing speeds in collisions with rolling stock[a]

Closing speed (mph)	*No. of collisions*	*Proportion of collisions* (%)
1–10	1	5
11–20	8	40
21–30	4	20
31–40	3	15
41–50	3	15
51–60	1	5

B Derailment speeds of freight trains

Derailment speed (mph)	*Proportion of derailments*	
	On plain track (%)	*Not on plain track* (%)
1–10	15	54
11–20	20	20
21–30	6	6
31–40	18	4
41–50	26	4
51–60	9	4
61–70	3	4
71–80	2	4
81–90	1	0

[a] Estimated from accident reports. Sample size = 20.
[b] After Taig (1980). Sample size = 300.

23.8.4 Derailments

Turning to derailments, these are generally less serious than collisions. The most severe derailments tend to be those which result in subsequent collisions. A study of derailments has been made by Taig (1980). He found that some 10% of derailments involve subsequent collision, 4% being with other rolling stock and 6% with other

objects. Taig also presents a graph showing data on the speed at which derailments occur. These data are given in tabular form by Davies and Lees, as shown in Table 23.24, Section B.

23.8.5 Fires

As stated above, in 1986 there were 53 fires recorded on freight trains. Small fires are a not uncommon occurrence, but very few become severe.

Fires may be classified as crash fires and non-crash fires. In the 187 accident reports for all trains initially reviewed for the FTA study, only one involved a non-crash fire, which was not on a freight train. By contrast, in the 38 reports of freight train accidents, there were 6 crash fires. Four of these resulted from collisions and two from derailments. All 6 fires were quite severe. On this basis, the ratio of crash to non-crash fires is of the order of at least 6:1. Since there were 34 crashes (collisions and derailments) in the survey, the probability of a fire given a severe crash is 0.18 (= 6/34).

23.8.6 Releases

Turning to accidents resulting in leaks, the ACDS report considers two categories of accident: (1) puncture of a tank wagon by collision or derailment and (2) failure or maloperation of the tank wagon equipment.

It considers each of the four study materials in turn. For motor spirit

Distance travelled = 10.2×10^6 tank-wagon-km/year

There were four puncture incidents in a 6.25-year period, giving:

Frequency of puncture of motor spirit tank wagon = 6.3×10^{-8} /tank-wagon-km

The report also mentions a BR estimate of puncture frequency of 10^{-8}/tank-wagon-km.

For the liquefied gases it refers to a study by ICI on incidents with the possible potential to cause puncture of a chlorine or ammonia tank wagon. In the 7-year period 1980–86 there were on tank wagons generally seven puncture incidents. These all occurred on tank wagons with 'thin' (6 mm) walls. It was estimated that for such incidents the average probability of puncture of a chlorine tank wagon was 0.0385 and that for an ammonia wagon 0.103. Then utilizing the figure of 47.4×10^6 tank-wagon-km travelled by all laden tank wagons each year, the following estimates are obtained:

Frequency of puncture of chlorine tank wagon = 0.9×10^{-9}/tank-wagon-km
Frequency of puncture of ammonia tank wagon = 2.5×10^{-9}/tank-wagon-km

The frequency of puncture of an LPG tank wagon was taken as the same as that for an ammonia wagon.

The other leak mode is failure or maloperation of the tank wagon equipment. These leaks were assumed to be relatively small. Estimates of the frequency of such leaks per 10–hour journey were made using fault trees, which are given in the report. The following results were obtained:

	Frequency of leak (leaks/journey)
LPG	0.83×10^{-8}
Chlorine	3.1×10^{-8}
Ammonia	1.3×10^{-8}

No evaluation was made for motor spirit, since the consequences were judged to be minor.

23.8.7 Release ignition

For the probability of the ignition of a leak of flammable material, BR incident reports showed that of five leaks over a period of 6.25 years, one ignited. The ACDS report bases its estimates partly on these data and data from fixed sites, and partly on judgement. It gives for small spills, whether of motor spirit or LPG, probabilities of 0.1 for immediate ignition, 0 for delayed ignition and 0.9 for no ignition. For large spills of motor spirit the corresponding probabilities are 0.2, 0.1 and 0.7 and those for large spills of LPG are 0.2, 0.5 and 0.3, respectively.

23.8.8 Marshalling yard incidents

The ACDS report also considers activities in marshalling yards. BR operates some 70 such yards, but the majority of movements of dangerous goods are by block trains which do not enter marshalling yards.

In the 8-year period to the end of 1987, there were two puncture incidents. These involved methanol tank wagons punctured in collisions, one by a coupling hook and the other by a shunting engine. On this basis, the report obtains a generic value for the puncture frequency of 'thin' walled tank wagons:

Frequency of puncture = 3.6×10^{-3}/yard-year

This implies similar levels of traffic at all yards.

For the four study substances, the proportions travelling by Speedlink service are: motor spirit, $< 1\%$; LPG, 28%; chlorine, 53%; and ammonia, $> 1\%$ (occasional wagon load returned to its origin).

Based on arguments relating to the differences between thin- and thick-walled tank wagons, the probabilities of puncture given an incident of the type just described were estimated as 0.01 for LPG and ammonia tank wagons and 0.005 for a chlorine tank wagon.

One of the busiest marshalling yards was selected for detailed study. The substance principally considered there was chlorine. The yard handles some 78% of the Speedlink chlorine traffic, or some 1500 chlorine tank wagons per year. It was estimated that the yard handles a total of 7990 laden tank wagons of hazardous substances per year.

The frequency of a chlorine leak due to a puncture of a tank wagon at this particular yard was then obtained as

Frequency of puncture of chlorine tank wagon

$$= 3.6 \times 10^{-3} \times 0.005 \times \frac{1500}{7990}$$

$$= 3.4 \times 10^{-6}/\text{year}$$

It may be noted that in deriving this figure for a busy yard it is the generic figure for puncture frequency for all yards which is used.

For leaks due to failure or maloperation of equipment, use was made of the data obtained in the *en-route* study, as given in Section 23.8.6. On the assumption that one-tenth of the total journey time is spent in the marshalling yard, the probability of a chlorine leak due to this cause was obtained as 3.1×10^{-9}/journey. Then

Frequency of leak due to equipment failure of chlorine tank wagon $= 1500 \times 3.1 \times 10^{-9}$
$= 4.6 \times 10^{-6}$/year

The other main study substance passing through marshalling yards is LPG. The yard studied handles some 200 laden wagons per year. However, LPG tank wagons are not actually marshalled. In view of this, the generic puncture frequency was reduced by a factor of 5. Then, taking the probability of puncture of an LPG tank wagon in an incident which would puncture a thin-walled wagon as 0.01, as given above, the frequency of an LPG leak due to puncture of a tank wagon at this particular yard was then obtained as:

Frequency of puncture of LPG tank wagon

$$= 3.6 \times 10^{-3} \times \frac{1}{5} \times 0.01 \times \frac{200}{7990}$$

$$= 4.6 \times 10^{-6}/\text{year}$$

23.8.9 Exposed population

The population exposed in a rail transport accident comprises the *en route* population and the other rail users, particularly passengers in other trains, together with the emergency services.

Meaningful assessment of the societal risk from rail transport requires the use of a reasonably refined population exposure model. The models used in the ACDS report are described in Appendix 17.

23.8.10 US environment

In the USA, the total railroad track mileage in 1981 was 327 000. From a survey of US and Canadian Class 1 railroads for 1983, the length of line surveyed was 145 881 which was 69.5% of the total track. This therefore gives for those two countries a total mileage of 209 900 for this class of track.

In 1986 there were in use in the USA some 183 000 tank cars, which comprised some 10% of the total fleet of freight wagons.

The NTSB *Annual Report* 1980 gives the railroad accident rate in 1979 for passenger and freight trains in the USA as 12.8 accidents per 10^6 train-miles. The 1981 *Report* gives for 1980 the following breakdown of causes of train accidents: track defects, 41%; mechanical/electrical failures, 17%; human factors, 28%; and other, 14%.

The main causes of accidents leading to loss of containment of hazardous materials from rail tank cars are derailments and collisions. One principal cause of such accidents is the state of the track and of the rolling stock.

23.9 Road and Rail Tunnels

Both road and rail systems include tunnels. In principle, there may be expected to be differences from open routes in respect both of the frequency and the consequences of incidents, but for there to be certain common features between road and rail tunnels.

Accounts of tunnels tend to be either descriptions of incidents or hazard assessments. Case histories involving tunnels are described in Section 23.21 and hazard assessment is described in Section 23.26.

23.10 Waterway Transport

The extent of waterway movement of hazardous materials is small in the UK, but it is considerable in Europe and the USA. The Rhine and the Mississippi are major arteries. Accounts of waterway transport have been given by H.P. Nelson (1964), Backhaus and Janssen (1974) and Ligthart (1980).

In the UK, British Waterways bylaws apply to the transport of dangerous goods on canals. It issues a document on the terms and conditions of acceptance.

In the USA, the responsibilities of the US Coast Guard extend to inland waterways. The US Army Corps of Engineers is also involved through its responsibility for waterfront structures and embankments, canals, bridges and dams.

Backhaus and Janssen quote the maximum size of LNG barge which might be used on the Rhine as 108 m long $\times$ 11.4 m broad. Alternatively, use might be made of four barges with a push tug with total dimensions 185 m long $\times$ 22.8 m broad.

The construction of the barge tends to vary with the type of material which it carries. In the USA, for example, for petroleum the barge shell is also the container wall, whereas for chlorine there are separate chlorine tanks within the barge structure.

A principal hazard of barge transport is collision. It is important to minimize the risk of this, not only when the barge is on the move but also while it is loading or unloading.

Another hazard of barge transport arises where barges are used to carry a variety of chemicals. While skilled people are generally available to assist at the loading point, the barge operator may well be on his own at the unloading point.

In the USA, the Coast Guard has attempted to improve the competence of barge crews by encouraging them to take specific training as chemical tankermen.

The NTSB annual reports describe measures to reduce collisions. In particular, efforts have been made to improve bridge-to-bridge communications.

A study of the hazards of transport of LPG on inland waterways has been described by Ligthart (1980). He states that serious risk arises only from collisions, although he qualifies this by excluding risks from cargo treatment, cleaning and repair.

23.11 Pipeline Transport

23.11.1 Regulatory controls and codes

The movement of hazardous materials by pipeline in the UK is regulated by the Pipelines Act 1962 and enforced by the Pipelines Inspectorate. The Act distinguishes between local pipelines (less than 10 miles long) and cross-country pipelines (greater than 10 miles long).

In the USA, pipeline transport is regulated by the DOT through the Natural Gas Pipeline Safety Act 1968 and related legislation for other hazardous materials. Relevant regulations include Pipeline Safety Program Procedures (Part 190) and Transportation of Natural and Other Gas by Pipeline: Minimum Federal Safety Standards (Part 192).

Some standards and codes for pipelines include BS CP 2010: 1970– *Design and Construction of Steel Pipelines in Land*, the ASME *Code for Pressure Piping* B31.4: 1974 *Liquid Petroleum Transportation Systems* and B31.8: 1975 *Gas Transmission and Distribution Piping Systems*, the IP *Pipeline Safety Code* (1982 MCSP Pt 6) and IGE/TD/1 *Steel Pipelines for High Pressure Gas Transmission* (IGE, 1984).

23.11.2 Hazard scenarios

For a pipeline carrying flammable gas some principal hazard scenarios are a jet fire and a flammable vapour cloud, leading to a flash fire or vapour cloud explosion, whilst for one transporting liquid the scenario is a liquid spillage leading to a pool fire or flowing liquid fire. The main hazard scenario for a pipeline carrying toxic gas or liquid is a toxic vapour cloud.

23.11.3 Pipeline economics

The economics of pipeline transport have been discussed by Lennart (1964). The cost breakdown for pipelines is quite different from that for other modes of inland transport. At that time, for pipelines the total costs were approximately 70% fixed costs and 30% variable costs, whilst for waterways, road and rail the fixed costs were 30, 15 and 5% and the variable costs 70, 85 and 95%, respectively. Moreover, the cost index n relating the capital cost C to the throughput P

$$C = kP^n \qquad [23.11.1]$$

where k is a constant, is very low. Lennart gives the capital cost of a 6 in. line as only about 45% more than that of a 4 in. line. Thus for the supply of an assured market at a fixed point a pipeline is a very attractive mode of transport.

23.11.4 Pipeline systems

In Western Europe and North America there are large pipeline systems carrying predominantly hydrocarbons. For the former, statistics on the pipeline network are given in *Performance of Oil Industry Cross-Country Pipelines in Western Europe: Statistical Summary of Reported Spillages—1991* (CONCAWE, 1991 4/92), which is part of an annual series.

In 1991, Western Europe had 210 service pipelines with a total length of 21 000 km. These pipelines carry some 593 million cubic metres of crude oil and refined products, giving a total movement of 101×10^9 m^3-km. Maps showing the pipelines in Western Europe as a whole and in particular areas are given in the CONCAWE report.

Statistics on pipelines in the USA are collected by the Federal Energy Regulatory Commission (FERC). Periodic reviews are given in the *Oil and Gas Journal*. In the review of the 1984 figures by True (1985), the mileage of interstate pipelines is given as, for gas, 258 204 miles and, for liquid, 173 922 miles.

Sources of information on pipeline failures also often contain information on the size of pipeline systems.

23.11.5 Pipeline design and operation

Pipelines are usually buried about 1 m below ground. Their environmental impact is therefore usually minimal and they can be difficult to detect even by aerial survey unless there are sufficient marker posts.

The extent to which the temperature of the gas in a pipeline varies depends on the depth at which it is buried, but for most pipelines in the UK the variation is small, although this is not always so in other countries.

The standards of construction and protection of pipelines have improved markedly over the years. The older pipelines were of mild steel or cast iron. The former have often corroded, while the latter have often withstood conditions better. There are cast iron brine mains, for example, which have remained in good condition. But cast iron has a relatively low resistance to impact and is not an ideal material for pipelines for hazardous substances.

Mild steel is now generally used for pipelines, but it is of much higher quality, being more uniform and better extruded or seam welded. Welds on the pipeline are more carefully done.

Pipelines are also much better protected. The older pipelines had no specific external protection. Then the wrapping of lines was developed, culminating in the present practice of using a coal tar/glass fibre wrap. But this was not the whole answer, because corrosion still occurred at points where the wrapping was badly done or was damaged or where there were line joints.

This problem has been largely overcome by the use of cathodic protection. Corrosion of steel involves iron passing into solution as an ion. This process may be reduced by impressing on the pipe a suitable voltage. It is still necessary to wrap the pipe, because the currents required with unwrapped pipe are excessive. But cathodic protection gives effective protection at defects and gaps on a wrapped pipe.

The modern method of external protection, therefore, utilizes a combination of wrapping and cathodic protection. With this system minimum external corrosion rates are obtained.

Internal corrosion depends on the material transported, but in many cases it is very low.

Pipelines are regularly inspected for corrosion, both external and internal. The internal surface of the pipe way be checked by instrumentation transported through the pipe by an 'intelligent pig'.

A code of practice for pipelines is provided by the *Pipeline Safety Code* by the IP (1982 MCSP Pt 6). This deals with the design, materials, land and rights of way, construction, testing, cathodic protection, operation, maintenance and emergency procedures.

The internal pressure of the pipeline should not be less than the normal maximum working pressure plus

any anticipated surge pressure. The minimum wall thickness for a straight pipe under internal pressure is determined by the formula

$$t = \frac{pD}{20 f_y a} \qquad [23.11.2]$$

where a is a design factor, D is the external diameter of the pipe (mm), f_y is the specified minimum yield strength (N/mm^2), p is the internal design pressure above atmospheric pressure (bar), and t is the design thickness of pipe wall (mm). The design factor a is taken as 0.72 for gas and liquid pipelines in remote areas.

Protective devices such as pressure relief devices and shut-down systems should be fitted to prevent the line pressure rising more than 10% above the internal design pressure and to deal with fluid expansion effects.

The Institute of Petroleum (IP) code describes a number of additional protective measures which may be provided to avert damage to a pipeline. They are: (1) increased earth cover; (2) increased coating strength; (3) an additional protective coating of concrete, provided this does not screen cathodic protection currents; (4) additional position markers on the surface; (5) increased pipe wall thickness; (6) provision of a casing sleeve; and (7), for above ground pipelines, provision of impact protection.

In some areas design of the pipeline against earthquakes assumes greater importance. Accounts of the seismic design of pipelines include those of Newmark and Hall (1975), Shinozuka, Takada and Ishikawa (1979) and Jinsi (1985).

Increasingly use is made of trenchless technology, in which a pipeline is installed, replaced or repaired without removing the earth above it. It is used particularly for water and gas distribution systems. An account of the set of technologies which come under this heading is given in *Introduction to Trenchless Technology* (International Society for Trenchless Technology, 1991). Whilst the techniques are applicable to distribution rather than transmission systems, they have been used for pressure piping and for quite large diameter pipes. Upsizing of pipes of 225 and 355 mm diameter is well established and pipes of up to 600 mm diameter have been done.

23.11.6 Hydrocarbon pipelines

The majority of pipelines carry flammable gases such as natural gas, ethylene or LPG or flammable liquids such as crude oil, oil products or NGL. It is to hydrocarbon pipelines that the account given so far mainly relates.

23.11.7 Ammonia pipelines

There are some very extensive liquid anhydrous ammonia pipeline systems, especially in the USA. The ammonia is mainly used by farmers in the corn belt as fertilizer.

Descriptions of the Mid-America Pipeline System are given by Rohleder (1969) and by Luddeke (1975) and of the Gulf Central System by Inkofer (1969).

The Gulf Central pipeline described by Inkofer has a 10 in. diameter trunk line 548 miles in length running south to north with two spur lines off it. One of these has 417 miles of 8 in. line and 235 miles of 6 in. line, the other has 234 miles of 8 in. line and 153 miles of 6 in. line. The design study was for a line operating at a pressure of 1440 psig (100 bar) and in the temperature range 35–75°F (2–24°C). Details of the design codes, materials and inspection methods are given by Inkofer.

The hazard of brittle fracture was given special consideration. Cases have occurred where brittle fracture has propagated along a pipeline at a velocity close to that of sound in the metal. Thus a large length of line could be affected. The maximum transition temperature for the pipeline was set at 0°F (−17.8°C), which is well below the normal operating temperature range. Above the transition temperature ductile shear failures may occur, but these were considered less serious.

The composition of the anhydrous ammonia is closely controlled to prevent attack on the pipeline. Impurities in ammonia, such as air or carbon dioxide, can cause stress corrosion cracking. This is largely inhibited, however, if the ammonia contains 0.2% water and this water content is specified as a minimum.

The pipeline has at approximately 10–mile intervals shut-off valves which can be closed manually. At the same points there are also check valves which prevent back flow from the line section ahead of the rupture point. At rather greater intervals there are pump stations with instrumentation which detects any sudden changes of pressure caused by a line break and stops pumps and closes automatic shut-off valves.

The situation arising in the event of a leak is considered by Inkofer. For a small leak he suggests that, in theory, the ammonia should freeze the surrounding ground, but this was queried in the discussion, where it was pointed out that practical experience indicates that small leaks of ammonia actually tend to dissolve in water and generate heat.

With a large leak due a major pipeline rupture, the line break detectors would stop the pumps and shut the isolation valves at the upstream pump station and the suction pressure controls would stop the pumps at the downstream pump stations, so that the pipeline break would be isolated to a single section.

There would be an initial high pressure spurt of ammonia as the pipeline pressure vented. The line pressure would then fall to that corresponding to the vapour pressure of ammonia at the line temperature, i.e. 107 psia at 60°F. Several other effects would further reduce the rate of discharge. Vapour locks would form at humps along the pipeline, and these would cause a back pressure due to the accumulated liquid heads created by each rise in the line ending in a vapour pocket. Flashing of vapour would cool the remaining liquid. The overall results of these effects would probably be that after the initial spurt of flashing liquid there would be a period of prolonged and spasmodic ejection of liquid and vapour.

The proportion of ammonia flashing off from saturated liquid at 60°F and 107 psia is approximately 10%. The remaining liquid would be cooled to −28°F and would form a pool. The evaporation from this pool would be in the range 1–7 lb/ft^2 h and thus fairly slow.

A 10–mile section of 10 in. line at 60°F contains 591 ton of ammonia and, assuming 90% of this forms a pool at −28°F, the resulting 24 990 ft^3 could form a pool of 12 495 ft^2 with a depth of 24 in., or one of 149 940 ft^2 with a depth of 2 in.

The pipeline is continuously monitored by a pipeline dispatcher. In the event of a line break he will know the location between the particular pump stations. He then

sends out a team to locate the break more precisely, to shut all isolation valves in the section affected and to open blowdown valves in order to encourage the formation of vapour locks. The basic procedure for containing the spillage is to dike around it. The line is then excavated and the rupture repaired. If necessary, stopple plugs are inserted into the line to shut off the flow.

The vapour from an ammonia line break is initially cold and heavier than air. It can travel in lethal concentration several miles. The dispersion of vapours from ammonia spillages was considered in more detail in Chapter 15.

The description given by Rohleder and by Luddeke of the Mid-America Pipeline system is broadly similar.

23.11.8 Chlorine pipelines

Pipeline transport of chlorine is much less extensive than that of ammonia. Chlorine lines are dealt with in *Chlorine Pipelines* (Chlorine Institute, 1982 Pmphlt 60). Further discussions are given by Danielson (1964) and H.P. Nelson (1964).

The chlorine may be transported either as vapour or as liquid. A vapour line should be operated with vapour phase only and a liquid line with liquid phase only. The situations which might give rise to mixed phase conditions should be identified and measures taken to avoid them.

The Chlorine Institute recommends that for any chlorine pipeline the maximum pressure should not exceed 300 psig (21 bar). However, this should not be construed as the design criterion. It recommends also that the maximum temperature at any section of the pipeline should not exceed 250°F (121°C).

The pipeline may be above or below ground. A line above ground is easier to monitor for external corrosion but an underground line may be safer in some circumstances. If the line is buried, consideration should be given to the frost line.

Internal corrosion is very low if the chlorine is dry, but is markedly increased by small quantities of water. It is essential, therefore, to design the line to facilitate drying out, to ensure that thorough drying is carried out and to keep the chlorine product dry.

Liquid chlorine has a very high coefficient of thermal expansion and it is necessary, therefore, to protect lines against hydrostatic rupture. The Chlorine Institute recommends the use of a pressure relief valve or bursting disc discharging to a receiver or safe area or, alternatively, the use of an expansion chamber. Nelson states that an expansion chamber should have a capacity of 20% of the line volume. If an expansion chamber is used, it should be properly operated and maintained, so that air in the chamber is not gradually replaced by chlorine.

The provision of a means for the control of line breaks is particularly important with a chlorine pipeline. Automatic shut-off valves may be installed for gas or liquid lines, while excess flow valves may be used as an alternative on liquid lines. A combination of both devices may be preferable for the liquid case.

23.11.9 Pipeline failures

For Western Europe the publication *Performance of Oil Industry Cross-country Pipelines in Western Europe 1991* (CONCAWE, 1992 4/92), one of a continuing series, gives details of pipeline failures.

In the USA there appears to be no single body which regularly publishes information on pipeline failure. Pipeline operators are required to report leaks to the Department of Transportation (DOT). The DOT issues an annual report on natural gas pipelines. Major pipeline accidents are investigated by the National Transportation Safety Board (NTSB). Both organizations periodically publish information on pipeline failures.

A survey on the *Safety of Interstate Natural Gas Pipelines* by the Federal Power Commission (FPC) (1966) gives information on failures in these pipelines in the 15½-year period from January 1950 to June 1965. The length of transmission pipelines covered was 204 730 miles in 1964. The number of failures recorded in the period was 1058 line failures, 121 compressor or metering station or other facilities failures, and 1115 field testing failures. Employees suffered 35 deaths and 135 injuries and non-employees 29 deaths and 87 injuries. Of the 64 deaths 42 arose from failures in

Table 23.25 *Failure of interstate natural gas transmission pipelines in the USA 1950–65: causes of failure (after Federal Power Commission, 1966)*

Pipeline punctured by plough, bulldozer, excavating shovel, road grader or other earth-moving equipment	279
Corrosion:	193
External	148
Internal	45
Weld failures	190
Action of the elements	84
Coupling failures	65
Damage during installation	58
Fatigue failures	35
Defective pipe	26
Thermal stress	21
External explosion	14
Miscellaneous	38
Unknown or unreported	55
Total	1058

Table 23.26 *Failure of interstate natural gas transmission pipelines in the USA 1950–65: failures by pipe diameter (after Federal Power Commission, 1966)*

Pipe diameter (in.)	*No. of failures reported*	*Failures per 1000 miles*	*No. of casualties reported*
0–5.0	141	10.6	4
5.1–10.0	324	11.6	25
10.1–15.0	132	9.0	9
15.1–20.0	278	12.0	43
20.1–25.0	97	5.9	35
25.1–30.0	62	2.6	31
>30.0	5	2.8	11
Unreported	19	–	9

Table 23.27 *Failure of oil pipelines in Europe 1972–76: causes of failure (after CONCAWE, 1977 9/77)*

Cause of failure	*1972–76*[a]	*1987–91*[b]
Mechanical failure:		
Construction	7	8
Material	14	7
Operational error:		
System	2	–
Human	2	2
Corrosion:		
External	34	8
Internal	2	5
Natural hazard:		
Subsidence	3	2
Flooding	–	–
Other	–	–
Third-party activity:		
Accidental	24	13
Malicious	–	2
Incidental	5	3
Total	93	50

[a] CONCAWE (1977 9/77).
[b] CONCAWE (1992 4/92).

lines and 17 from failures in compressor or metering stations or other facilities. The causes of the line failures are analysed in Table 23.25. The relations between the number of failures and of casualties over the $15\frac{1}{2}$-year period and the pipe sizes are given in Table 23.26.

The *Annual Report on the Administration of the Natural Gas Pipelines Safety Act of 1968* by the DOT for 1974 states that in 1974 there were 335 000 miles of natural gas gathering and transmission pipelines, and that in the period 1970–74 there were 2093 failures. From these data the failure rate for such pipelines was 1.25×10^{-3} per mile per year. In this period there were eight fatalities to employees and the same number for non-employees. Causes of the 460 failures in 1974 are broken down as follows:

Cause	*Proportion* (%)
Damage by outside forces	59.5
Corrosion	17.0
Construction defect or material failure	17.6
Other	5.9

The annual report on pipeline failures up to 1976 by CONCAWE (1977 9/77) states that between 1972 and 1976 the combined length of oil industry pipelines increased from 15 800 to 18 100 km and that in the period 1972–76 there were 93 spillages. From these data, assuming an average of 17 700 km of pipeline over the period, the failure rate obtained for such pipelines is 1.05×10^{-3}/km-year. The causes of the 93 failures are categorized in Table 23.27, first column. The corresponding report up to 1991 by CONCAWE (1992 4/92) states that in 1991 there were some 21 000 km of pipeline and that in the period 1987–91 there were 50 spillages. Assuming an average of 20 000 km of pipeline over the period, the failure rate obtained is 0.5×10^{-3}/km year. The causes of the 50 failures are categorized in Table 23.27, second column.

Further information on gas pipelines operated by the British Gas Corporation (BGC) has been given by Knowles, Tweedle and van der Post (1977). They state that since 1970 all faults on the transmission system have been recorded and that up to August 1977 there had been 309 repairable incidents, of which 73 were defined as 'lost gas' incidents. The following classification is given:

Mechanical interference (including coating damage)	204
Corrosion (internal and external)	32
Other faults (including faulty seal on pig trap door, leaking flanges, cathodic protection pad weld crack, etc.)	56
Girth weld	9
Pipe defect	5
Ground movement	3
Total	309

Table 23.28 *Failure of British Gas Corporation gas transmission pipelines 1970–77: failures by pipe wall thickness (after Knowles, Tweedle and van der Post, 1977)*

	Wall thickness (in.)					
	≤0.374		*0.375–0.499*		*0.500–0.625*	
	No.	*No./1000* mile-year	*No.*	*No./1000* mile-year	*No.*	*No./1000* mile-year
Total No. of interference incidents	98	3.36	60	2.96	34	1.70
No. of incidents due to excavating machinery	69	2.36	33	1.63	18	0.90
Total No. of leaks	15	0.51	4	0.19	2	0.10
No. of leaks due to excavating machinery	5	0.17	0	0	1	0.05
Mileage at risk		3579		2480		2439

Table 23.29 *Failure of oil pipelines in Western Europe 1975–80 (after Blything 1984 SRD R326, from CONCAWE)*

A No. of failures by pipe diameter and cause

Cause	*Pipeline diameter* (mm)						
	150–275	*300–360*	*400–460*	*500–560*	*600–700*	*>800*	*All diameters*
External corrosion	14	5	3	0	0	0	22
Third party	17	5	5	1[a]	0	0	28
Mechanical	3	0	1	4	1	4	13
Natural hazard	1	2	1	1	2	0	7
All causes	35	12	10	6	3	4	70

B Overall failure rates by pipe diameter

Pipeline diameter		*Length* (km)	*Frequency of failure* (failures/km-year)
(mm)	(in.)		
150–275	6–10	4967	1.2×10^{-3}
300–360	12–14	2598	7.7×10^{-4}
400–460	16–18	3118	5.3×10^{-4}
500–560	20–22	2402	4.2×10^{-4}
600–700	24–30	2358	2.1×10^{-4}
>800	>32	2757	2.4×10^{-4}
All diameters			6.3×10^{-4}

C Size of defects[b]

Pipeline system	*Cause of failure*	*Defect diameter range* (mm)	*No. of incidents*	*Spillage volume* (m^3)
WE oil pipelines, 1978	Third party activity	< 50	1	2.5
		50–100 (80)	2	58
	Mechanical	< 50	1	19
		>100	1	2000
Canadian oil pipelines	Third party activity	< 50 (40)	3	50, 28, 24
		50–100 (76)	4	12, 48, 953, ?
		>100 (151)	3	64, 935

[a] Failure caused by loss of support due to indirect third party activity.
[b] Also some Canadian data.

The interference incidents are further broken down as shown in Table 23.28. The total number of leaks includes broken connections and piercing of the carrier pipe, while the number of leaks due to excavating machinery covers piercing of the carrier pipe only.

A failure rate of 5×10^{-3}/mile-year for chlorine pipelines was used by Westbrook (1974) in his assessment of the hazard of this mode of chlorine transport, as described in Chapter 18.

A study of pipeline failure rates in which the prime concern was with failure of offshore pipelines in the North Sea has been described by de la Mare and Andersen (1981). The work draws on the data sources already mentioned, i.e. the DOT for the USA, CONCAWE for Western Europe and British Gas for the UK, and also the US Coast Guard (USCG) for the Gulf of Mexico, Gaz de France (GdF) and the E&P Forum for the Arabian Gulf. The authors quote the following failure rates: CONCAWE, for onshore crude oil and product pipelines in Western Europe 1966–76, 0.39 $\times 10^{-3}$/km-year for crude oil, 1.11 $\times 10^{-3}$/km-year for products, and overall 0.69 $\times 10^{-3}$/km-year; British Gas, for its gas transmission network 1970–77, 0.65 $\times 10^{-3}$/km-year; Gaz de France, for its gas transmission network 1967–77, 3.3 $\times 10^{-3}$/km-year; USCG, for offshore pipelines (6–18 in.) in the Gulf of Mexico, for oil 17.4 $\times 10^{-3}$/km-year and for gas 12 $\times 10^{-3}$/km-year. The North Sea had recorded two failures, giving a failure rate of 0.7 $\times 10^{-3}$/km-year, but with 95% confidence limits 0.067–2.5.

The authors conclude that: the failure rates of pipelines appear similar even where the fluid handled and the environment are different; that the failure rates of oil pipelines depend on the diameter; that about half the failures can be attributed to external factors; and that pipelines tend to exhibit wearout failure. On this latter point, they quote CONCAWE data for the times to the first, second and later failures, and analyse these data to demonstrate that wearout failure occurs.

Another study of pipeline failure, confined to oil lines, is that given by Blything (1984 SRD R326), who considers pipeline failures in the USA, Canada and

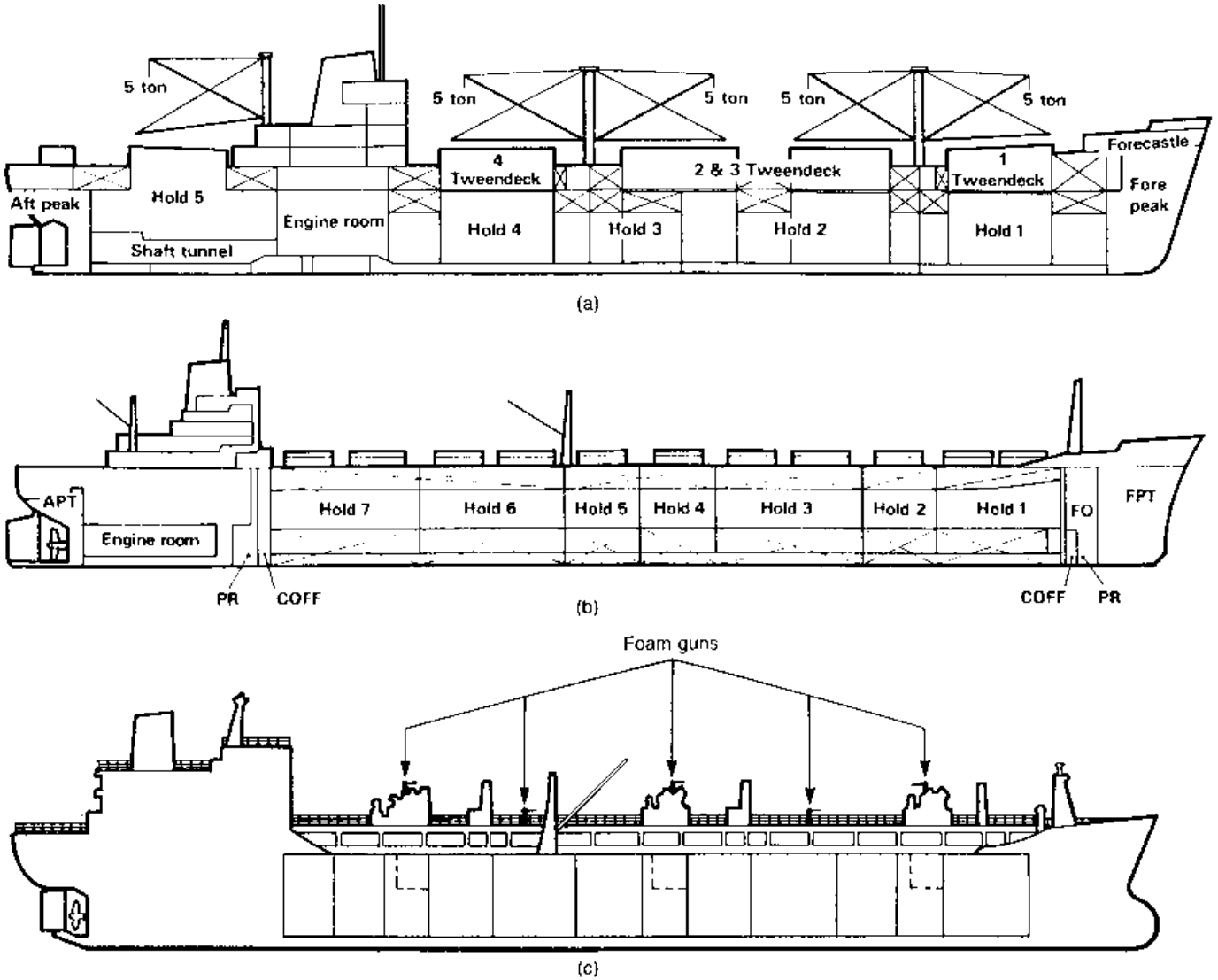
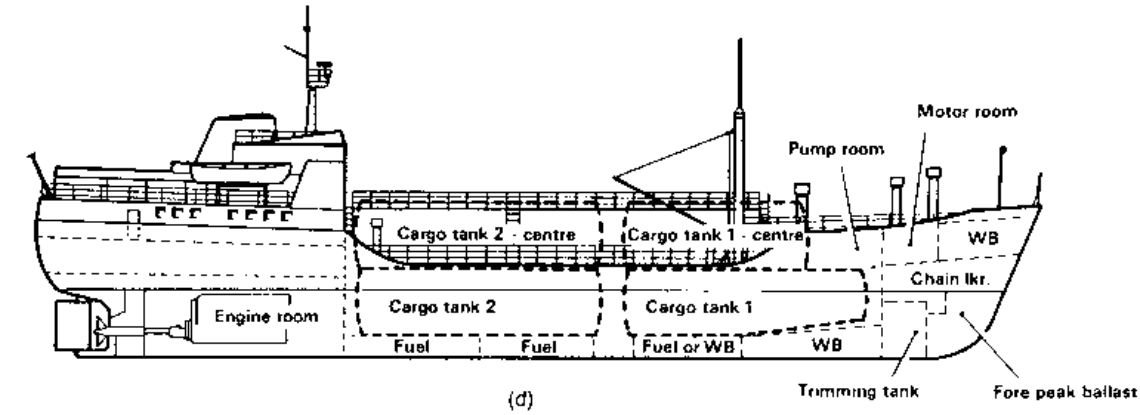


Figure 23.5 *Some typical vessels (Home Office, 1985* Manual of Firemanship *Bk 4): (a) cargo ship; (b) oil tanker; (c) chemical tanker; (d) and (e) LPG carriers; and (f) LNG carrier (Courtesy of HM Stationery Office. Copyright. All rights reserved)*



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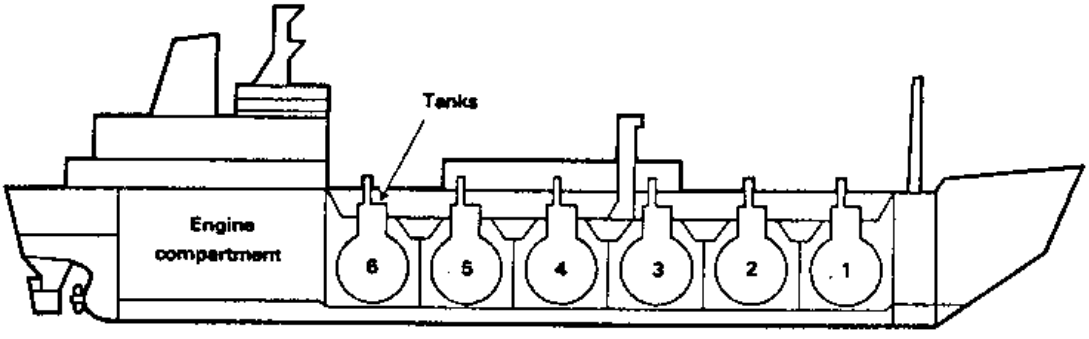

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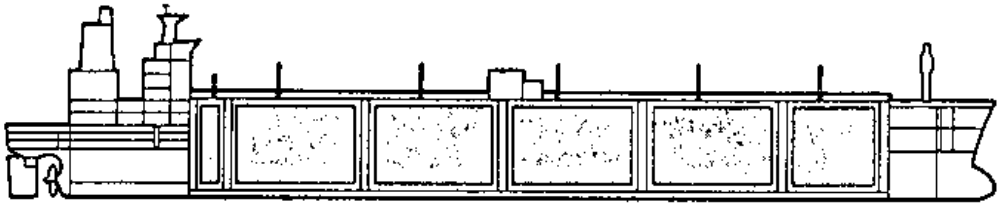


(f)

Figure 23.5 *continued*

Western Europe, using data from the DOT and NTSB, the Canadian Petroleum Association (CPA) and CONCAWE, but mainly from the latter. Some of their analyses of the CONCAWE data for Western Europe are given in Table 23.29. Section A of the table gives the number of failures by pipe diameter and cause, Section B the overall frequency of failure by pipe diameter and Section C the size of the defects and spills.

Section A shows that the most important causes of failure are third party activity (TPA) and external corrosion. Both are dependent on the diameter of the pipe. The other two causes are less significant and less diameter dependent. External corrosion is also a function of the fluid carried and is most frequent on lines conveying heavy fuel oil (HFO). This mode of failure is often by pinhole leaks and tends to have a low potential for major hazard.

Section B of the table shows that the overall failure rate of the pipeline decreases with increasing pipe diameter.

The data on size of defects were somewhat sparse. Some 21 incidents were found in the data for Western Europe and Canada where defect size was recorded. Of these, 15 were caused by third party activity. The defects were either holes or partial penetrations which failed at a later date. For some of these incidents it was possible to estimate the size of the spill. Data for these incidents are given in Section C of Table 23.29. Details on each of the 21 incidents are given by Blything.

These two reports give a wealth of further information on pipeline failures. As described, the main cause of failure in pipelines is interference, or third party activity. In particular, damage occurs to pipelines from earth-moving and excavating equipment. Most pipelines can be punctured by the tooth of a mechanical excavator with the possible exception of very large mains, which have a thickness of about $\frac{1}{2}$ in. In rural areas this may arise particularly from ditching and land drain work, in urban areas from work on services such as water, gas, electricity and sewage. It is essential, therefore, for the pipeline operator to keep a close watch on activities which may give rise to the hazard and for him to liaise with the authorities involved with planning and utilities. Moreover, it should be borne in mind that the person who needs to know is the excavator operator, and the organizations concerned should understand their responsibilities to ensure this.

23.12 Marine Transport: Shipping

Marine transport is distinguished from the other modes of transport in a number of ways. These includes its international nature, which has many aspects; the size of the cargoes carried; and the marine environment.

General accounts of marine transport are given in the ACDS *Transport Hazards Report* (1991), *Safer Ships, Cleaner Seas* (Donaldson, 1994) (the *Donaldson Report*) and *The Carriage of Bulk Oil and Chemicals at Sea* (Rawson, 1994), which may be supplemented by the references cited below.

23.12.1 Shipping industry

Marine safety needs to be viewed against the background of the shipping industry and its particular characteristics. An account of this background is given by Gilbert (1994). Since 1945 international trade has experienced an explosive growth. One consequence has been a massive increase in vessel size. Contrary to what might be expected, the industry is a 'low entry' one. As Gilbert states 'In boom times, banks and financial institutions have been only too willing to lend money to almost anyone who could submit a reasonable prospectus'.

Most ships are custom built. The owner identifies a particular market. Shipyards are then prepared to tailor the design to the owner's requirements. Ships are built with single or double hulls, single or twin screws, and slow or medium speed engines, in combination with a wide variety of cargo, ballast and fuel systems. This is in marked contrast, for example, with the situation pertaining in the design of aircraft.

Another characteristic feature is manning. Crews often contain many nationalities, some of whom may have difficulty in communicating with each other.

Shipping is vulnerable to the international economic cycle, so that in bad times large numbers of ships are laid up and sections of the industry are barely viable. This increases reluctance to incur expenditure on safety.

The international nature of the industry and the resistance of a large part of it to effective controls has meant that international agreements have tended to represent the lowest common denominator.

23.12.2 Hazard scenarios

A marine accident may pose a major threat not only to life but also to the environment.

A loss of containment of a material may occur due to damage to the cargo tanks or during loading and unloading operations. A serious hazard to life may arise from the release of a large quantity of flammable or toxic liquefied gas onto water, where it will vaporize rapidly, in or near a port. The USCG has commissioned studies of the hazard arising in this situation, such as the one by Eisenberg, Lynch and Breeding (1975). However, although much feared, this hazard has not so far been realized on a large scale.

Shipboard fire and explosion is another serious hazard and one which does occur periodically. The initiating event may be a fire in the engine room, the pump room, a cargo tank or elsewhere. Or it may be an explosion in the engine room or cargo tank. A particular hazard exists if the ship carries explosive substances. Some of the most devastating explosions have occurred from the explosion of ammonium nitrate cargo.

Loss of cargo also presents a threat to the environment. Here oil cargoes present a particular threat, since oil is carried in large quantities and is liable to do damage to the marine environment which it is difficult to prevent.

23.12.3 Ship design

Fundamentals of ship design are described in *Principles of Naval Architecture* (Comstock, 1967), *Basic Ship Theory* (Rawson and Tupper, 1968–), *Basic Naval Architecture* (Barnaby, 1969) and *Mechanics of Marine Vehicles* (Clayton and Bishop, 1982). Liquefied gas carrier design is described in *Liquefied Gas Handling Principles on Ships and in Terminals* (SIGTTO, 1986/3). Accounts of ship design and construction with special reference to hazards are given in *Incidents Involving Aircraft, Shipping and Railways* (Home Office, 1985 *Manual of Firemanship* Bk 4) and in the *NFPA Handbook*.

A ship is essentially constructed as a box girder formed by the hull and the main deck and strengthened by members such as the keel, frames, bulkheads and other decks.

Cargo ships are of two broad types: (1) dry cargo ships and (2) bulk cargo ships. The first group are general purpose dry cargo ships carrying smaller quantities in packages, drums and tank containers, and include general purpose ships, container ships, and roll-on/roll-off (RoRo) passenger (and cargo) ships. The second group are ships for the bulk transport of (1) crude oil, (2) petroleum products, (3) LNG, (4) LPG and other liquefied gases and (5) chemicals.

Table 23.30 *Typical ship movements in a major waterway (Sanders and Aldwinckle, 1987) (Courtesy of Gastech)*

Ship size ($\times 10^3$ GRT)	*Ship type*				
	Oil tanker	*Chemical tanker*	*Gas carrier*	*Other*	*All*
0–1	42	0	9	1 064	1 115
1–2	22	153	21	1 374	1 570
2–4	74	62	28	1 591	1 755
4–6	130	48	64	2 044	2 286
6–15	316	65	227	8 043	8 651
15–30	702	33	165	4 361	5 261
30–80	2 317	78	0	3 621	6 016
80 >	537	0	0	556	1 093
Total	4 140	439	514	22 654	27 747

Figure 23.5 illustrates some typical vessel designs. Figure 23.5(a) shows a cargo vessel; Figure 23.5(b) an ore/bulk/oil (OBO) carrier; and Figure 23.5(c) a chemical tanker, or tank vessel. An oil tanker is broadly similar to the latter in respect of the layout of the holds, but tends to be very large. Figures 23.5(d) and (e) show two types of LPG carrier, and Figure 23.5(f) shows an LNG carrier.

Older tank vessels have pump rooms, one forward and one aft between the engine room and the last cargo tank. In newer vessels the pump rooms are eliminated by the use of deep well pumps.

A gas carrier, for liquefied gases, has cargo tanks which may operate at atmospheric pressure or higher pressure. Such tanks may be integral with the vessel or independent of it.

Further treatment of ship design is deferred to Section 23.16, where a description is given of LFG carriers and chemical tankers.

An account of the influence of the chemicals carried on ship design and operation, as reflected in the provisions of the International Martime Organization (IMO) codes, has been given by Farrell (1982).

23.12.4 Ship operation

The transport of hazardous materials by ship calls for an approach to loss prevention very similar to that required for land installations. The management and the systems and procedures are crucial. There should be identification and assessment of hazards. An effective instrument system, with trips where necessary, is required. There needs to be a variety of fire protection measures. Operations such as loading and unloading should be carried out in accordance with specified procedures. There should be an inspection system with appropriate record keeping akin to that used for pressure systems. The equipment should be well maintained and control exercised over modifications. There should be a permit-to-work system. Personnel should be thoroughly trained in all these aspects.

Operations of particular relevance here are the loading and discharge of cargo and the operations on cargo tanks. These are discussed in Sections 23.14–23.17.

Inspection of tanks is covered in *Guidance Manual for the Inspection and Condition Assessment of Tanker Structures* (ICS, 1986/5), *Guidelines on Surveys Required by the 1978 SOLAS Protocol, the IBC Code and the IGC Code Fire Test Procedures* (IMO, 1987 IMO-858), *Inspection Guidelines for Bulk Carriers* (OCIMF, 1989/8), *Inspection Guidelines for Ships Carrying Liquefied Gases in Bulk* (OCIMF, 1990/10) and *Condition Evaluation and Maintenance of Tanker Structures* (ICS, 1992/12)

23.12.5 Particular chemicals

An important category of substances moved by sea is liquefied gases. These are not confined to LNG and LPG or even other hydrocarbons, but include a number of other major chemicals.

A gas tanker is often designed to carry not only LPG but also ethylene, ammonia and vinyl chloride monomer as the principal cargoes, but the list of products may well be more extensive. A cargo list for such a tanker is given by Puklavec and Lindeneau (1985):

Ethylene	*n*-Butane, *i*-butane	Mixtures of ethylene oxide/propene oxide
Ethane	Butadiene	Acetaldehyde
Propene	Butylenes	Monoethylamine
Propane	Vinyl chloride monomer	Methyl chloride
Ethane/propane mixtures	Isoprene monomer	Dimethylamine
Anhydrous ammonia	Propene oxide	Diethyl ether

Other products are carried in general chemical tankers, or chemships.

The *Bulk Carrier Code* (IMO, 1990 IMO-100) has both ship type and additional requirements which are a function of the chemical carried.

An important class of chemical in sea transport is monomers. Monomers such as vinyl acetate need to be inhibited during transport. The effectiveness of inhibition depends on the oxygen concentration and problems can

occur from polymerization due to low oxygen concentration. An account of inhibitors for vinyl monomers has been given by Douglas, von Bramer and Jenkins (1982) and of the specific problem of vinyl acetate inhibition by D.W. Butcher and Sharpe (1983).

Other accounts of the transport of particular chemicals include that of R. W. Macdonald (1977) on chlorine and that of Brumshagen (1983) on carbon dioxide.

23.12.6 Ship movement

The control of ship movement in restricted waters is necessary because the risk of collision or grounding is greater and the consequences may often be more serious. The arrangements for ship control vary in different countries but many of the principal waterways have some form of movement control. This may vary from speed restrictions and a requirement for pilotage to a full system akin to that used in air traffic control.

There have been a number of studies of ship movement and of ship traffic control systems. The USCG has undertaken a programme of work on this topic. Table 23.30 shows typical ship movements in a major waterway as given by Sanders and Aldwinckle (1987). An account of ship movement at the approaches to Rotterdam has been given in a study of ship incident probabilities by Ligthart (1980). The speed restrictions required by the Port of London Authority as described in the *Canvey Reports* are discussed in Appendix 7.

The proportion of 'errant vessels' in traffic lanes on the UK continental shelf has been studied by Technica (1985). This report was a follow-up to previous work on ship–platform collisions, which showed that the main risk is from errant vessels. One of the main points made is that errancy is not restricted to particular vessels, crews or captains, but may occur at some time in any vessel, although the frequency of such periods will vary between vessels. The findings were that the proportion of vessels which are errant at a given time is about 1.6%, both with good visibility and with bad, but that the proportion likely to recover from being on an imminent collision course fell for vessels of $< 40\,000$ DWT from 78% in good visibility to 8% in poor visibility and for vessels of $> 40\,000$ DWT from 39% to 4%, respectively.

23.12.7 Factors enhancing risk

In recent years there have been a number of developments which have combined to increase the risk of vessel failure. An account is given by Gilbert (1994). Among these developments are the massive increase in size of vessels. This is not just a matter of increase in the hazard. Gilbert states 'Many of these cape-size vessels (100 000 to 170 000 DWT) have been lost over the last two years due to suspected structural failure'.

Structurally, important factors have been the reduction in scantlings, the use of high tensile steels or inferior coatings, increased stress caused by high capacity loading systems and poor lay-up provisions.

Gilbert describes the three main modes of vessel failure: fire, collision and grounding. He also draws attention to the risk from piracy, which in some regions is not negligible. He states 'In some instances, fully-loaded tankers have been left to steam at full speed in enclosed waters with no-one on the bridge, because pirates have locked up or otherwise restrained the crew'.

23.13 Marine Transport: Regulatory Controls

23.13.1 International regulatory controls and codes

The international marine transport of dangerous goods is the concern of the International Maritime Organization (IMO) (formerly the International Maritime Consultative Organization (IMCO)). This organization has a fairly complex structure of committees, which include the Maritime Safety Committee (MSC) and the Marine Environment Protection Committee (MEPC).

Other interested bodies include the International Chamber of Shipping (ICS), the Oil Companies International Marine Forum (OCIMF) and the Society of International Gas Tanker and Terminal Operators (SIGTTO), together with International Association of Ports and Harbours (IAPH), the International Petroleum Industry Environmental Conservation Association (IPIECA) and the International Tanker Owners Pollution Federation (ITOPF).

Accounts of the international controls and codes for the marine transport of dangerous goods are given in the *NFPA Handbook* (Cote and Linville, 1986) and by the ACDS (1991).

Some principal international conventions and conferences include the International Convention for the Prevention of Pollution of the Sea by Oil 1954 (OILPOL), the International Conference on Revision of the International Regulations for Preventing Collisions at Sea 1972, the International Convention of Prevention of Pollution from Ships 1973 (MARPOL), the International Convention on the Safety of Life at Sea 1974 (SOLAS), the International Convention on Training, Certification and Watchkeeping for Seafarers 1978 (STCW), and the Convention on the International Maritime Organization 1984.

The resolutions of the periodic Safety of Life at Sea (SOLAS) conferences are a continuing source of provisions in the international system of control. The SOLAS Convention 1974 contains mandatory requirements concerning carrier safety. Chapter VII of the Convention deals with dangerous goods.

Some principal IMO codes include the *Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk* (the *BCH Code*) (IMO, 1993 IMO-772), the *International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk* (the *Bulk Carrier Code*, or *IBC Code*) (IMO, 1990 IMO-100) and the *International Maritime Dangerous Goods Code* (the *IMDG Code*) (IMO, 1992 IMO-200).

There are three IMO codes for liquefied gas carriers: the *Code for Existing Ships Carrying Liquefied Gases in Bulk* (IMO, 1976 IMO-788), the *Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk* (IMO, 1983 IMO-782) and the *International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk* (the *Gas Carrier Code*, or *IGC Code*) (IMO, 1993 IMO-104). The first code applies to ships built up to 1976 and the second generally applies to ships built after 31 December 1976 and before 1 July 1986.

Guidance issued by the ICS and other bodies includes *Safety in Chemical Tankers* (ICS, 1977/1), *Safety in Oil Tankers* (ICS, 1978/2), *Safety in Liquefied Gas Tankers* (ICS, 1980/3), *Liquefied Gas Handling Principles on Ships and in Terminals* (SIGTTO, 1986/3), *International Safety*

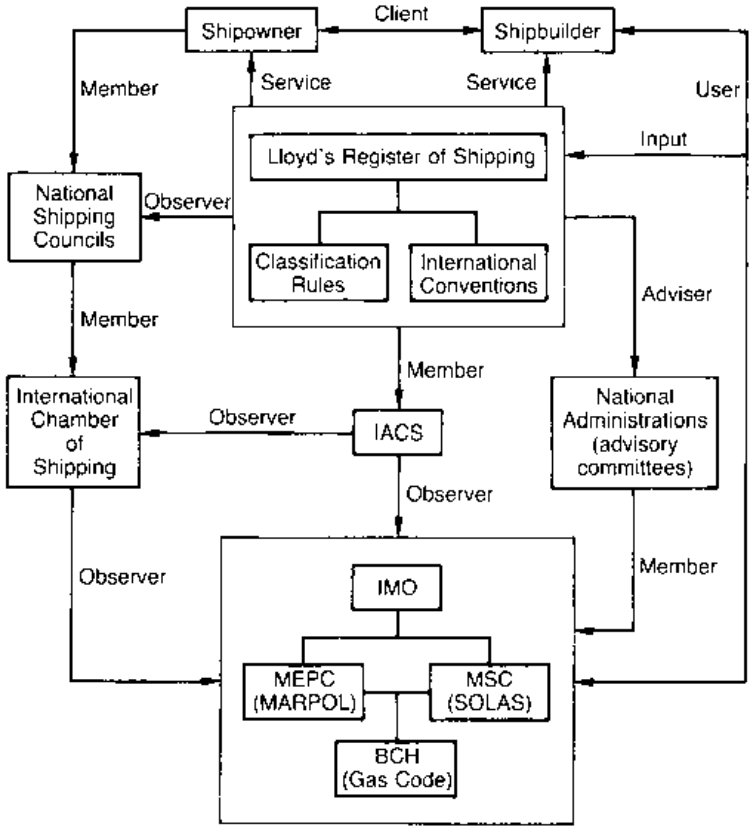


Figure 23.6 *Relationship of the Lloyds Register classification society with regulatory bodies and the liquefied gas shipping community (McLean and Cripps, 1986) (Courtesy of Gastech)*

Guide for Oil Tankers and Terminals (*ISGOTT*) (ICS, 1991/11), the *Tanker Safety Guide (Chemicals)* (ICS, 1971/13) and the *Tanker Safety Guide (Liquefied Gases)* (ICS, 1993/14).

23.13.2 Paris Memorandum

The responsibility for enforcement of international agreements on marine safety lies with the state in which the vessel is registered (the flag state). Standards are variable and, as a secondary measure, the states at whose ports the vessel calls (the port states) are empowered to carry out inspections and to detain the vessel whilst repairs are done. This latter arrangement is governed by the Paris Memorandum of Understanding on Port State Control of 1982 (the Paris Memorandum, or Paris MOU). An account of this system is given in the *Donaldson Report* (Donaldson, 1994), described below, and its operation is reported in the annual reports of the Paris Memorandum.

23.13.3 Classification societies

In international shipping an important role is played by the classification societies, of which the best known is Lloyds of London. An account of the work of Lloyds is given by McLean and Cripps (1986). The relationship of Lloyds to many of the international organizations mentioned is shown in Figure 23.6.

The classification societies operate a system of classification rules, as described below. In addition, the major societies are authorized by over 125 administrations to apply the requirements of specified IMO conventions and to issue certificates of fitness. The Lloyds Register requirements for gas ship construction and class maintenance are outlined in Figure 23.7.

23.13.4 Classification rules

Major sets of rules at Lloyds are the *Rules and Regulations for the Classification of Ships* and the *Rules for Ships for Liquefied Gases*.

An account of Lloyds' Classification Rules is given by J. Smith (1994). The hull of a ship must be able to withstand the forces due to still water and specified wave-induced loads. It must possess the local strength to resist buckling, fatigue, yielding and brittle fracture. In the Classification system this is achieved by compliance with the Rule materials requirements, hull arrangements and scantling formulations. The Rules are intended to provide basic proven design methods whilst leaving freedom to innovate. They prescribe design methods

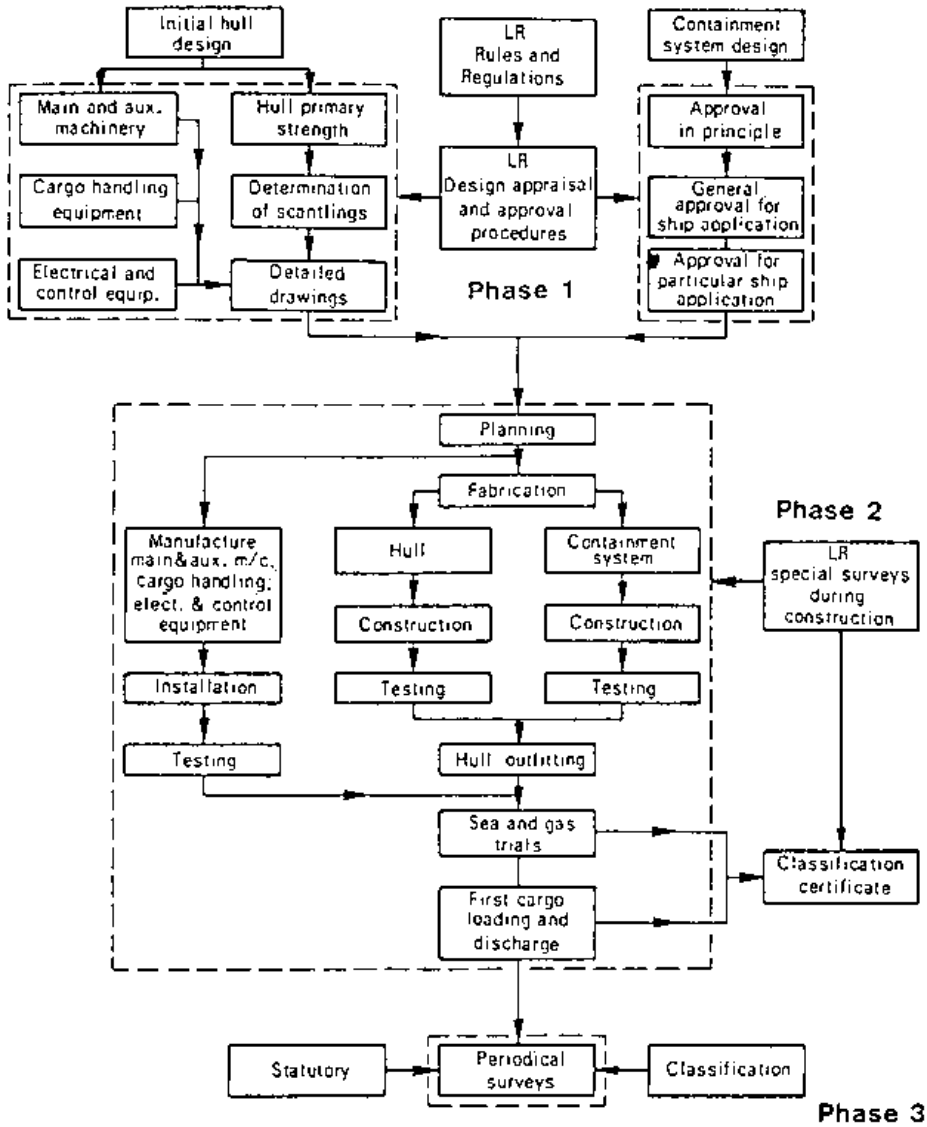


Figure 23.7 *Lloyds Register requirements for liquefied gas ship construction and class maintenance (McLean and Cripps, 1986) (Courtesy of Gastech)*

for the ship's hull and certain other features and equipment. The system recognizes the principle of 'equivalence' and permits an alternative combination of arrangements and scantling, provided that it can be demonstrated to be of equal strength.

23.13.5 UK regulatory controls

In the UK the transport of hazardous materials by sea is regulated by the Department of Trade (DoT) through the Merchant Shipping Act 1965 and succeeding Merchant Shipping Acts and through a series of regulations which include the Merchant Shipping (Cargo Ship Construction and Survey) Regulations 1984, the Merchant Shipping (Fire Protection) Regulations 1984, the Merchant Shipping (Gas Carrier) Regulations 1986, the Merchant Shipping (BCH Code) Regulations 1987, the Merchant Shipping (IBC Code) Regulations 1987 and the Merchant Shipping (Dangerous Goods and Marine Pollutants) Regulations 1990.

The Department of Transport (DTp) maintains a Standing Advisory Committee, which has for some years issued the *Recommendations for the Carriage of Dangerous Goods in Ships*, commonly known as the '*Blue Book*', covering variations from and additions to the *IMDG Code* judged appropriate for the UK. The 1990 edition of the *IMDG Code* with the 25th set of

amendments provides comprehensive coverage of matters dealt with in the *Blue Book*, which is now superseded.

British law has held that the act of sending to sea an unseaworthy vessel is a misdemeanour. The Merchant Shipping Act 1979 replaced the wording 'unseaworthy' by 'dangerously unsafe'. The Merchant Shipping Act 1988, Section 30, gives powers to prosecute the owner and master of unsafe British ships in any port world-wide and of unsafe foreign ships in British ports.

In the UK, enforcement of the Paris Memorandum is the responsibility of the Marine Safety Agency (MSA). Accounts of the regulatory framework in the UK are given by Hodges (1994) and K. James (1994).

23.13.6 Seaworthiness

In British maritime law, an important concept in marine safety, as described by Hodges (1994), is that of the 'seaworthy' vessel, legally defined as one which is in 'a fit state as to repairs, equipments, crew and in all other respects, to encounter the ordinary perils of the sea'. The definition is thus limited to the perils 'of the sea' rather than 'on the sea'.

Aspects of seaworthiness which have been the subject of court judgements include: the ship's suitability to carry its cargo, or its cargoworthiness; its design and construction; its machinery, equipment and navigational aids; the sufficiency and competence of the crew; the sufficiency and quality of the fuel; and the stability and stowage of the cargo.

The seaworthiness of a ship is a particular aspect of its safety. For example, a deficiency in the medical supplies would detract from safety, but would not render the ship unseaworthy.

23.13.7 *Donaldson Report*

The *Braer* disaster in 1993 was the subject of an inquiry reported in *Safer Ships, Cleaner Seas* by Lord Donaldson (1994) (the *Donaldson Report*). The report reaffirms the duty of the flag state to enforce controls on the safety of vessels registered with it, but states that: 'There is clear evidence that some Flag States are failing in their responsibilities …'. It recommends various measures to strengthen the controls exercised by the port states.

23.13.8 Safety case

Following the Piper Alpha incident and the *Cullen Report*, the new UK offshore regulatory regime is based on formal safety assessment and the safety case. This has led some to advocate a similar regime for ships at an international level. The question of a regime for ships based on a safety case is discussed by J. Smith (1994).

The critique of a safety case for an individual ship has two main aspects, the potential benefits and the practical difficulties. With regard to benefits, the question concerns the extent to which the design and operation of the ship itself involves the type and degree of hazard for which the safety case methodology is suitable. The other question is the practicality of applying a safety case regime to international shipping, particularly given the difficulties experienced in enforcing even a relatively straightforward prescription-based regime.

There may well be benefits to be had from generic formal safety assessment studies. The question of formal safety assessment of ports, sea lanes, etc., is another matter and is well established.

23.13.9 US controls

In the USA, ships trading in US waters have to meet the requirements of the US Coast Guard (USCG). The USCG have responsibility for ensuring the safety both of US vessels and US ports.

The USCG requirements for gas carriers are given in the Code of Federal Regulations, Title 46. The requirements for new ships are given in Part 154 and those for existing ships in Part 38. New ships are essentially those which meet the IMO *Gas Carrier Code* and existing ships are those which do not. An account of the USCG controls has been given by Rowek and Cook (1986).

The USA has now taken action to raise the standard of ships calling at its own ports. The Oil Pollution Act 1990 (OPA) provides that from the year 2010 all such vessels must have double hulls.

23.13.10 Pressure for change

Shipowners are currently subject to a number of pressures to enhance the safety of vessels. Some of these are described by Rawson (1994). They include: IMO initiatives, unilateral legislation such as the OPA 1990 and the Paris Memorandum; the requirements of the classification societies and of the insurers, which are gradually tending to become more stringent; and the growth of litigation. Regulatory controls are thus increasingly being reinforced by economic pressures. There is, however, a long way to go.

23.14 Marine Transport: Ports and Harbours

23.14.1 Regulatory controls and codes

Ports and harbours are the controlled through the Docks Regulations 1988 and dangerous substances are controlled through the Dangerous Substances in Harbour Areas Regulations 1987 (DSHA). Guidance is given in HS(R) 27 *A Guide to the Dangerous Substances in Harbour Areas Regulations 1987* (HSE, 1988) and GS 40 *The Loading and Unloading of Flammable Liquids and Gases at Harbours and Inland Waterways* (HSE, 1986). Also applicable are the regulations for fixed sites, including the Notification of Installations Handling Hazardous Substances Regulations 1982 (NIHHS), the Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH), the Dangerous Substances (Notification and Marking of Sites) Regulations 1990 and the Planning (Hazardous Substances) Regulations 1992.

Interested organizations include the International Association of Ports and Harbours (IAPH) and the Independent Tank Storage Association (ITSA).

The DSHA Regulations are divided into ten parts: (1) interpretation and application, (2) entry of dangerous substances into harbour areas, (3) marking and navigation of vessels, (4) handling dangerous substances, (5) liquid dangerous substances in bulk, (6) packaging and labelling, (7) emergency plans and untoward incidents, (8) storage of dangerous substances, (9) explosives, and (10) miscellaneous and general.

Some principal regulations of the DSHA Regulations are: Regulation 6 on the notice of entry of dangerous

substances; Regulation 7 on harbour masters' powers of prohibition of dangerous substances, etc.; Regulation 18 on precautions against fire and explosion; Regulation 19 on the fitness of vessels; Regulation 20 on permission for transfer between vessels; Regulation 21 on safety precautions for loading, unloading and transfer; Regulation 26 on the preparation of emergency plans by harbour authorities; Regulation 27 on emergency arrangements at berths; Regulation 28 on untoward incidents; Regulation 29 on the storage of dangerous substances; Regulation 30 on storage tanks; Regulation 31 on the storage of freight containers, etc.; Regulation 32 on the parking of road vehicles; Regulation 34 on the need for an explosives licence; Regulation 37 on the security of explosives; Regulation 41 on deteriorated explosives; Regulation 43 on the power of harbour authorities to make bylaws; and Regulation 44 on enforcement. Regulation 28 deals both with the action in the event of untoward incidents and on reporting of such incidents. Regulation 34 defines the cases where there is need for an explosives licence; Regulations 37–42 on explosives apply irrespective of whether a licence is required.

HS(R) 27 contains in Appendix 3 guidance on emergency plans and in Appendix 4 a checklist of duties under the Regulations, covering some 18 categories of person, including: the harbour authority, berth owner and berth operator; the harbour master; the harbour and the berth explosives security officers; the masters of vessels; the operators of barges and harbour craft, road tankers, rail tank wagons, and storage; consignors; drivers; and employers and the self-employed.

COP 18 expands on some of these requirements, giving more details on aspects such as the information to be provided by incoming tankers, which includes the substances carried, the equipment available such as an inert gas system, defects on the ship and the expected time of arrival (ETA); the control of rail traffic in harbour areas; the ship–shore transfer of dangerous liquids; precautions against fire and explosion, which include the elimination of ignition sources and the provision of fire fighting facilities; storage tanks for dangerous substances; the handling, storage and security of explosives; the discharge of harmful dusts and vapours to the atmosphere; and emergency planning, at both harbour and berth level. It contains an appendix giving a checklist for ship–shore transfer.

23.14.2 Port design and operation

Accounts of the handling of hazardous materials at ports have been given by Gebhardt (1980, 1989) and by P. Lewis (1981).

Cargo is handled at a port in four basic modes:

(1) bulk materials;
(2) packaged goods;
(3) containers;
(4) roll-on/roll-off.

The characteristics of these modes are discussed by Lewis.

Some aspects of the design and operation of ports relevant to the handling of hazardous materials include:

(1) ship traffic control;
(2) ship–shore transfer;
(3) emission control;
(4) hazardous area classification;
(5) jetty fire protection.

Control of ship traffic is considered in Section 23.12, ship–shore transfer is considered in Section 23.14.3, and jetty fire protection is discussed in Section 23.14.4.

Some emission of flammable gas is unavoidable during loading operations. As with land-based plant it is necessary to consider the dispersion of such gas. Similarly, it is necessary to have a hazardous area classification of the ship and the jetty.

23.14.3 Ship–shore transfer

The loading and discharge of cargo is a hazardous operation over which strict control needs to be exercised. Accounts are given in *Liquefied Gas Handling Principles on Ships and in Terminals* (SIGTTO, 1986/3), *Guidelines for the Alleviation of Excessive Surge Pressure in ESD* (SIGTTO, 1987/4) (the SIGTTO *ESD Surge Pressure Guidelines*) and *Recommendations and Guidelines for Linked Ship/Shore Emergency Shutdown of Liquefied Gas Cargo Transfer* (SIGTTO, 1987/5) (the SIGTTO *ESD Guidelines*) and by Gebhardt (1980), Armitage (1983), B. White and Cooke (1983), Holdsworth (1985) and Whitmore and Gray (1987).

Loading arms are covered in *Design and Construction Specification of Marine Loading Arms* (OCIMF, 1987/5). There is also guidance on manifolds (OCIMF, 1987/7 and 1991/12) and on hoses (OCIMF, 1991/11)

Accounts of the development of the SIGTTO guidelines on ship–shore transfer and emergency shut-down (ESD) are given by Holdsworth (1985) and Whitmore and Gray (1987).

The transfer of hazardous materials between ship and shore during loading and unloading depends on the effective operation of a number of systems which include:

(1) mooring system;
(2) loading arms;
(3) pumping system;
(4) pressure relief.

Some hazards of ship–shore transfer are:

(1) ship movement;
(2) leakage;
(3) overfilling;
(4) overpressure;
(5) pressure surge.

Mooring systems have already been discussed. A good mooring is required to ensure that the ship does not break away during transfer. It is also desirable that the motion of the ship be minimal.

There are various arrangements for connecting the ship's cargo tanks to the land terminal. Types of loading arm in common use include Chiksan loading arms and Kvaerner arms.

In order to prevent leakage, pressure surge, overfilling or overpressure of tanks, it is necessary to design for these hazards and to establish a suitable link between ship and shore which allows orderly shut-down to be carried out.

There should be a trip system so that shut-off can be effected in the event of a serious leak. The operating pump should be interlocked to stop if the shut-off valve closes.

If shut-off is too rapid, pressure surge is liable to occur and can be very damaging. The prevention of pressure surge in this situation is an important feature of the SIGTTO arrangements (SIGTTO, 1987/4 and 5). It has been discussed by Armitage (1983).

Measures need also to be taken to avoid overfilling and overpressure. Particular consideration should be given to the relief arrangements at the receiving end in relation to the delivery flow and pressure in order to ensure that overpressure does not occur.

The operating arrangements, discussed by Gebhardt (1980), are equally important. The transfer operation should be planned. There need to be sufficient personnel available on ship and on shore. At each end there should be an engineer in charge of the transfer. There should be good communication between ship and shore and the principal tasks of the transfer operation should be co-ordinated.

The SIGTTO *ESD Guidelines* (SIGTTO, 1987/5) describe a standardized link connecting ship and terminal ESD systems to communicate and initiate ESD safely and rapidly. They give in an appendix a practical example of an intrinsically safe ship–shore ESD link system.

The SIGTTO *ESD Surge Pressure Guidelines* (SIGTTO, 1987/4) describe the hazards of surge pressures and give sets of guidelines common to ships and terminals and others specific to the ship or the terminal. The former cover (1) safe transfer rates, (2) valve characteristics and closure times, (3) pipeline design pressure and pipeline anchors, (4) linked ship and terminal ESD systems, and (5) operational factors. The guidelines also include an engineering treatment of surge as applied to loading systems and unloading systems and design approaches to alleviate surge pressures, including (1) pump shut-down/diversion of flow and (2) surge pressure relief.

A checklist for ship–shore transfer has been given by B. White and Cooke (1983).

Guidance on ship–ship transfer is given in *Ship to Ship Transfer Guide (Liquefied Gases)* (ICS, 1980/4) and *Ship to Ship Transfer Guide (Petroleum)* (ICS, 1988/7)

23.14.4 Jetty fire and fire protection

An account of fire and fire protection at jetties has been given by Dicker and Ramsey (1983). The minimization of the fire hazard at a jetty depends not only on the specific fire protection measures but also on the general standard of design, operation and maintenance. The ship–shore transfer systems are one important feature here. The arrangements for dealing with leaks and spillages are another.

The objectives of fire protection may be summarized as:

(1) prevention of fires and explosions;
(2) extinguishment of small fires;
(3) control of fires that cannot be extinguished;
(4) cooling of vulnerable equipment;
(5) protection to permit escape;
(6) protection to permit ship/shore access.

It may not always be possible to extinguish a fire and in such a case the fire should be controlled and vulnerable equipment such as tanks, loading arms, pipelines and manifolds on shore or on ship kept cool.

The resources available on site should be such that an effective initial response to the fire can be mounted whilst the arrival of the outside fire services is awaited.

The approach to fire protection at a jetty is broadly similar to that on a plant. Basic elements include:

(1) control of leaks;
(2) control of ignition sources;
(3) fire control system;
(4) means of escape;
(5) means of access.

The fire control system includes:

(1) fire warning system;
(2) fire detection system;
(3) fixed fire fighting system;
(4) mobile fire fighting system;
(5) fire water supply system.

First consideration should be given to avoidance of leaks of flammable materials. Potential leak sources should be reviewed and appropriate action taken.

A source of flammables which is peculiar to jetties is flammable vapour vented from ship cargo tanks.

Most of the common sources of ignition may be present at a jetty. These include hot work, repair work, vehicles and smoking. There are also activities specifically associated with shipping which may cause ignition such as use of ship's galley equipment, repair work involving hammering or paint chipping, blowing of funnel uptakes or boiler tubes, or disconnection of ship–shore cargo pipelines.

Control of ignition sources should be based on a hazardous area classification. The *Area Classification Code for Petroleum Installations* by the IP (1990 MCSP Pt 15) gives guidance on hazardous area classification for jetties.

In this connection Dicker and Ramsey deprecate the use of a blanket approach in which flameproof equipment is applied without detailed study. They suggest that there is benefit to be gained from the source of hazard method which gives a better understanding of the potential leak sources. These authors also state that it has to be accepted that complete elimination of all sources of ignition from hazardous areas is not practicable in all circumstances at jetties.

It is usual to provide a variety of means for fighting and controlling fire. For cargoes of crude oil or flammable liquids the principal fire fighting agent used is foam, which is applied by foam monitors. Low expansion foam is the most suitable for a jetty since it has a reasonable range. Fixed foam monitors may be used and may be remotely controlled. They may be supplemented with mobile monitors. Foam is usually not recommended for burning liquefied gas fires, since the gas tends to penetrate the foam blanket.

If the fire is on a gas or vapour leak, the preferred course of action is to stop the leak. Extinguishing the flame without stopping the leak risks allowing the creation of a flammable vapour cloud which may give a more violent flash fire or vapour cloud explosion.

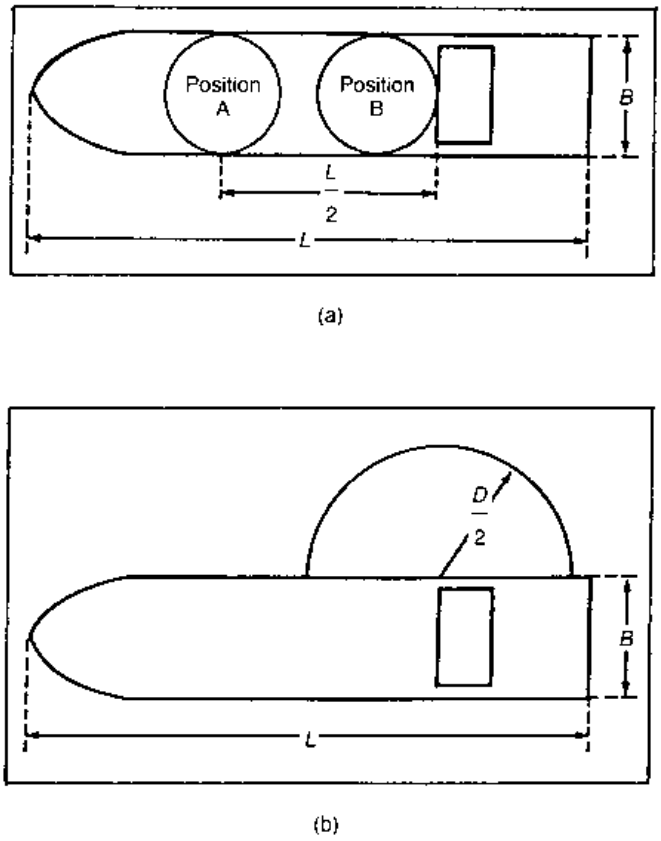


Figure 23.8 *Design basis fires for an LNG/LPG carrier (S. Stephenson and Coward, 1987): (a) position of fires on the deck; (b) position of a fire on the sea (Courtesy of Gastech)*

Water monitors are used to cool exposed items, as already described. In the jetty situation, cooling of the gangways between the ship and shore is important for escape.

The capacity of the foam and water systems should match the fire fighting requirements. For large vessels these can be appreciable.

Effective fire control depends on co-ordination between shore and ship. One aspect of this is the compatibility between the ship and shore fire mains. It is necessary to ensure that connection of the ship's fire water system to that on shore does not result in overpressurization.

Another aspect is the responsibility for fire control in the early stages. Since in the event of fire the ship's crew need to attend to other actions, particularly the closure of pipelines and actions to prevent fire spread, it may be advantageous to control initial fire fighting from the shore.

There should be good ship–shore communications. These are particularly important in the jetty situation, not only for fire fighting but also for assisting escape. Regular exercises of the fire control system should be held.

Accounts available of the fire protection arrangements at major terminals include those that of the arrangements at Rotterdam by Vossenaar (1975), at Wilhelmshaven by Hartlich (1977) and at Hamburg by Gebhardt (1980, 1989).

Vossenaar quotes for the port of Rotterdam traffic of 34 000 ships and 170 000 barges per annum. The area fire brigade has some 500 full time firemen who deal each year with about 5000 fire and other emergencies. The fire brigade is equipped with high capacity pumps capable of delivering 4000 l/min. There are also 14 fire boats, most of which have an output of 15 000 l/min and carry substantial quantities of foam, as well as a fire fort, a converted ferry, with a 30 m tower.

Hartlich gives a detailed account of the construction of the Mobil terminal at Wilhelmshaven and of the fire-fighting arrangements. There are separate fire water systems which draw on sea water and on the refinery fire water supply. The sea water pumps are protected against pack ice and freezing.

The foam supply is estimated to last 60 minutes, supplying 2×5000 l/min and 3×800 l/min foam monitors. The monitors can be operated from the control

Table 23.31 *Design basis fires for an LNG/LPG carrier (S. Stephenson and Coward, 1987) (Courtesy of Gastech)*

A Fire on deck[a]

Fire position	*View factor*	*Wind velocity* (m/s)	*Flame tilt* (°)	*Target heat flux* (kW/m^2)
A	0.06	0	0	5
A	0.06	5	34	11
A	0.06	10	46	12
B	0.35	0	0	33
B	0.35	5	34	37
B	0.35	10	46	44

B Fire on sea[a]

Size of carrier (m^3)	*B* (m)	*L* (m)	*Spill rate* (kg/s)	*D* (m)	*View factor*	*Atmospheric transmissivity*	*Target heat flux* (kW/m^2)
2 500	13	80	10	9.5	0.08	0.95	8
2 500	13	80	100	30	0.19	0.95	18
2 500	13	80	1 000	95	0.24	0.95	23
25 000	25	200	10	9.5	0.04	0.95	4
25 000	25	200	100	30	0.13	0.92	12
25 000	25	200	1 000	95	0.22	0.90	20
25 000	25	200	10 000	300	0.25	0.90	22
125 000	42	280	10	9.5	0.02	0.90	2
125 000	42	280	100	30	0.08	0.90	7
125 000	42	280	1 000	95	0.18	0.88	16
125 000	42	280	10 000	300	0.24	0.85	20

[a] Flame height/diameter ratio H/D = 3 in zero wind. Atmospheric conditions: good visibility, 10% humidity. Emissive power of fire = 100 kW/m^2

building and also from other auxiliary control points. Use of the refinery mobile foam monitors extends the period of foam application to some 2 hours.

The foam monitors have a range of 85 m. This is not enough to give coverage of the whole deck of a supertanker, but such ships have their own systems.

The foam induction rate is 5%. Devices are used to keep the induction rate constant at variable water flows. The foam compound is highly viscous and its flow velocity is low so that large diameter mains are necessary. These have a holdup of some 10 000 l of the compound.

There are water monitors with an output of 3000 l/min for cooling ships' gangways and hulls. Dry powder systems also are provided for fighting fires on platforms and around manifolds.

Two of the jetties at this terminal are on an island. For this situation it is necessary to provide facilities somewhat similar to those on an oil platform, such as lifeboats and fireproof shelter.

Somewhat similar arrangements at the Shell terminal at Kattwyk at Hamburg-Harburg are described by Gebhardt.

Evacuation of the ship in the event of a spillage of liquefied gas may be assisted by the use of a water curtain to reduce the level of thermal radiation to which the crew are exposed. A study of such a system has been described by S. Stephenson and Coward (1987).

Two principal scenarios are considered, the first, shown in Figure 23.8(a) being for a fire on deck, and the second, shown in Figure 23.8(b), for a fire on the sea. The fire considered in the first case was a pool fire with diameter equal to the width of the ship and sufficient fuel for burning to be maintained and evacuation to be necessary, and the second case considered was a fire on a continuous spill onto the sea. A model for heat transmission through water curtains was developed and embodied in the computer program PRINCE, as described in Chapter 16.

The target heat fluxes for the two design basis fires are shown in Table 23.31. It is concluded that the water curtain considered would reduce the heat flux received by the human targets from 16 to 5 kW/m^2 and that this provides a significant contribution to safe evacuation.

23.15 Marine Transport: Shipboard Fire and Fire Protection

An account of fire and explosion on board ships of all kinds is given in *Fire Aboard* (Rushbrook, 1979). This work lists all recorded ship fires between 1800 and 1977 and describes in detail many of the principal incidents. It describes the general maritime legislation and that pertaining to fire-related aspects of ship design and construction. It covers fire protection aboard ship, including fire-proofing of ships, fire equipment on ships and fire fighting on ships, and fire protection of ports and offshore structures.

The fire-proofing of ships is governed by the Merchant Shipping (Construction) Rules 1965 and, for cargo ships,

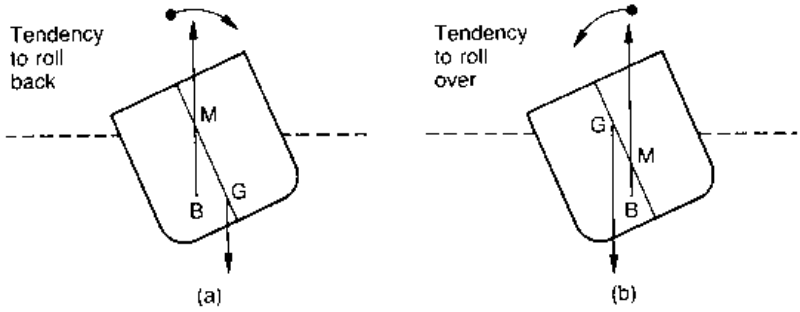


Figure 23.9 *Effect of the centre of gravity on ship stability: (a) tendency to roll back; (b) tendency to roll over. B, centre of buoyancy; G, centre of gravity; M, metacentre*

the Merchant Shipping (Cargo Ship and Survey) Rules 1965. Rushbrook's account follows closely the requirements of these rules and covers watertight doors, fire resisting and fire retarding divisions, fire resisting materials, electrical equipment and installation, oil fuel installations, ship structure, and construction aspects such as means of escape and facilities to shut off forced ventilation. He also treats under this heading fire detection systems and sprinkler systems.

Requirements for fire fighting equipment on ships are contained in the Merchant Shipping (Fire Appliances) Rules 1965. Features covered by Rushbrook include: fire pumps and pump siting, fire water hydrants, fire hoses and hose reels, and portable fire extinguishers; fire fighter's breathing apparatus, including hose reel and trolley compressed air apparatus, and high pressure air charging equipment; fire smothering arrangements, including inert gas generators, funnel gas inerting systems, steam smothering systems and high pressure water sprays; fire detection and alarm systems; and certain special topics such as foam installations in mechanical spaces and crankcase monitoring.

Rushbrook emphasizes the need for training for the whole range of tasks required in ship operation. He quotes legal cases establishing the employer's obligation to provide training. Aspects of fire training mentioned include fire patrolling and fire fighting, but the issue is much wider than this.

A detailed account of fire fighting under different conditions is given by Rushbrook. Situations considered include fires in holds, in accommodation space, in refrigerated space, in fore and after peaks, and in engine rooms and machinery spaces.

He gives a detailed discussion of the problem of fires in holds. In general it is a golden rule of fire fighting to hit the fire fast and hard, but this is not necessarily the right approach to a hold fire. There is a tendency to open up the hold too soon. It may often be better to develop a coherent plan of attack and make suitable preparations and, if there is an inerting system, to activate it and let it do its work. There are exceptions, however; immediate action is necessary when the cargo is nitrates, sulphates or explosives.

If quantities of water are pumped into the ship to fight a fire, they may lead to instability. Stability is determined by the relation between the ship's centre of gravity and its centre of buoyancy. The centre of gravity is the point at which its weight may be taken to act, in the vertical direction. The centre of buoyancy is the centre of gravity of the water displaced. If a vertical line is drawn through the centre of gravity of a body floating in a liquid and a second vertical line is drawn through the centre of buoyancy when the body is slightly displaced from its equilibrium position, the two lines meet at a point known as the metacentre. If the centre of gravity is below the metacentre, the ship is stable and will right itself, as shown in Figure 23.9(a), but if the centre of gravity is higher, the ship is unstable and tends to capsize, as shown in Figure 23.9(b). One solution to the problem of instability due to fire water is the use of an ejector, but this also has its limitations.

23.15.1 Cargo tanks

The problem of flammable cargoes and of the associated fire and explosion hazards is discussed in detail in *Petroleum Tankship Safety* (Page and Gardner, 1971).

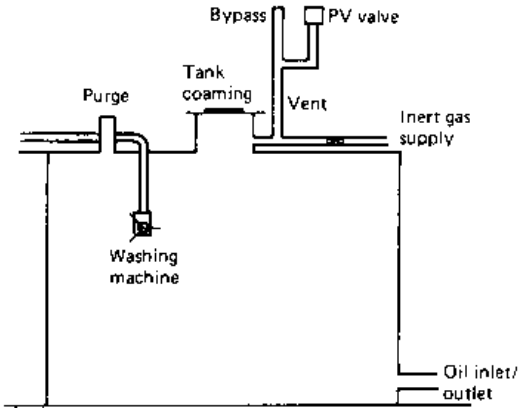


Figure 23.10 *Typical cargo tank system on a petroleum tanker*

Although oil tankers at any rate are now required to have inert gas systems to prevent tank fires, an understanding of such fires remains important.

A typical tank system for a petroleum cargo ship is shown in Figure 23.10. The tank is designed to operate at a pressure of about 1.17 bar (2.5 psig) and can withstand about 1.24 bar (3.5 psig). If this latter pressure is exceeded, the decks and bulkheads may give way.

The tank is fitted with an atmospheric vent which has a pressure/vacuum (PV) valve for normal operation and a bypass for loading. The PV valve is set to maintain the pressure within narrow limits, 0.14 bar (2 psi) above atmospheric and 0.035 bar (0.5 psi) below atmospheric.

During loading the bypass is used, since the flow of gas necessary to equalize pressure is too great for the PV valve to handle. At other times the bypass is kept shut.

It is important that vapour issuing from the vent during loading should not form a hazardous flammable or toxic cloud and it is desirable, therefore, for it to leave the vent at a velocity sufficient to promote mixing with the air. If loading is slow, the vapour may issue slowly and may accumulate. This problem may be overcome by fitting a minimum efflux velocity valve.

There may or may not be an inert gas system which is used to prevent the occurrence of a flammable mixture in the tank. If no such system is provided, there may be a flammable atmosphere during certain stages of the transport cycle. The air mixture found in the space depends on the volatility of the liquid.

Assuming that this is a volatile oil, which in this context means an oil above its flash point, then if the tank is clean and gas free, and contains only air before loading, the mixture in the vapour space will go from a too lean to a too rich mixture during loading. The diffusion of the vapour is slow, however, and a period of hours or even days may elapse before the space is saturated. Initially there may be a range of conditions in the tank from a too lean mixture near the roof to a too rich mixture in the vapour layer just above the liquid. During loaded passage the atmosphere remains too rich. The vapour concentration falls again, however, during unloading. If the rate of unloading is high, the turbulence of the air entering tends to give a homogeneous atmosphere in the vapour space, while if it is too low, there may be layering. At the end of unloading, the atmosphere may be too lean, flammable, or too rich, depending on the volatility of the oil. The same applies if the tank is left empty but dirty during passage.

If the oil is involatile, then in principle a flammable mixture does not form, but this may occur if the oil is heated to assist pumping so that it rises above its flashpoint or if the tank contains traces of a volatile oil.

The pressure in the tank is maintained close to atmospheric by ejecting air through the vent bypass during loading, by the operation of the PV valve during loaded passage and by letting air in through the vent bypass during unloading.

In addition to loading and unloading operations, there are also those of tank cleaning and gas freeing. Tank cleaning is carried out by washing machines. If at all possible, it should be done with a too lean atmosphere. Gas freeing is effected by steaming out or by diluting the atmosphere with air drawn through it by extractor fans or steam eductors or blown in by windsails.

It is essential to eliminate all source of ignition. Some sources which are particularly relevant are as follows:

(1) direct heat –
  (a) cigarettes,
  (b) welding,
  (c) hot soot;
(2) mechanical sparks –
  (a) metal tools,
  (b) cigarette lighters,
  (c) heavy objects;
(3) chemical energy –
  (a) metal smears,
  (b) spontaneous combustion,
  (c) autoignition,
  (d) pyrophoric iron sulphide;
(4) electrical equipment;
(5) static electricity.

Heavy objects which may produce a spark if they fall inside the tank include washing machines and anodes of cathodic protection systems.

Static electricity may arise from several causes. Charge separation occurs as the oil flows through the loading pipe. It also occurs if the oil is splashed or sprayed or if the turbulence of the oil raises up water droplets which then settle through the oil. Charge recombination may then occur due to an earthed probe such as a washing machine, the use of an ullage tape or the presence of a floating metal object such as a tin can or piece of wood with metal bolts. Precautions include the elimination of earthed probes and floating objects and the adoption of suitable ullage measuring arrangements.

The use of steam for tank cleaning may also involve a static electricity hazard, but this is minimized by using only fixed apparatus bonded to the ship's structure, keeping the steam velocity low and eliminating earthed probes.

Further details of the precautions necessary in loading and unloading and in tank cleaning and gas freeing are given by Page and Gardner.

If there is an inert gas system, this may be used to maintain an inert atmosphere in the tank. The inert gas produced with good combustion practice and after cooling and purification has a composition of approximately 3% oxygen, 13% carbon dioxide and 84% nitrogen. Under less ideal combustion conditions the gas may contain carbon monoxide or more oxygen.

Prior to loading the tank is purged with inert gas down to an oxygen concentration of about 5%, the purge gases being discharged through the purge pipe. During loading the gas displaced by the liquid is discharged through the vent bypass. The pressure in the tank during passage is maintained by the PV valve. When the liquid is unloaded, more inert gas is allowed into the tank to prevent a vacuum developing. After unloading the tank may be cleaned with its atmosphere still inerted.

An inert gas–vapour mixture is rather similar to a too rich mixture – it may become flammable if it is diluted with air. Situations in which this may happen include venting to atmosphere and rupture of the tank.

The types of explosion which can occur in a tank vary. One factor is the volume of flammable mixture. This is a maximum when there is no liquid in the tank and a flammable mixture fills the whole space, a situation

which may occur after loading or during cleaning. Another factor is the power of the explosion. If the mixture is close to its flammability limits and the flame speed is correspondingly low, the explosion tends to be low powered and the pressure rise gradual, so that the tank ruptures and the burning gases escape without further pressure rise in the tank.

There are several situations in which a low powered explosion may give rise to a more powerful one. The initial explosion may overheat adjacent tanks. If the original mixture was close to the upper flammability limit, the explosion may cause dilution by air to give a more flammable concentration, while if the mixture was close to the lower limit, the explosion may vaporize more liquid to yield again a more flammable concentration.

Usually tanker explosions occur without prior warning, but sometimes the possibility of an explosion can be assessed from the nature of the flame issuing from the deck openings. A yellow-orange flame accompanied by black smoke indicates that the tank atmosphere is too rich and the flame will not pass back into it. A snapping, blue-red, nearly smokeless flame signifies that the tank contains a flammable mixture and that the flame may pass back. In this latter case an explosion is imminent and the deck should be evacuated immediately.

A fire on deck does not usually cause a cargo tank to explode, provided that the tank is completely closed.

There is a trend towards the provision on tankers of an accommodation 'citadel' in which the crew are protected against fire in the cargo tanks, the cargo deck area, the engine room or the pump room. Measures are taken to reduce the risk of fire in the citadel itself. The ventilation system of the citadel and of the engine room should be such as to minimize the hazard from the entry of noxious gases.

23.15.2 Static electricity

Static electricity as a cause of ignition of flammable mixtures in cargo tanks has already been considered in general terms. Detailed studies of the hazard have been carried out in support of the chemical industry's case against compulsory inerting. Accounts of this work have been given by H.R. Edwards (1983) and by M.R.O. Jones and Bond (1984).

Edwards describes a series of experiments to determine whether the operations of loading, water washing and steam cleaning are capable of giving potentials sufficient to cause an incendive spark. Five trials were done on four vessels.

The minimum potentials required to produce incendive sparks were estimated as follows. For loading the required potential was taken as 20 kV based on work by Rees (1981) and by Strawson and Lyle (1975b). For water washing, work by van de Weerd (1975) indicates a required potential of 15 kV, but a value of 10 kV was adopted. The same value of 10 kV was also taken as the required potential for steam cleaning.

In the loading experiments the liquid used had a relatively low resistivity and high potentials were not obtained, the maximum surface potential being 3.4 kV. Estimates were made for other conditions using the method of Carruthers and Wigley (1962). It was estimated that the maximum surface value for a very high resistivity liquid (1 pS/m) would be 16.5 kV. The surface potential is a function, however, of tank size and this maximum value is obtained only with tanks smaller than those normally used. With such a liquid there is also the option of limiting the charge rate. It is concluded that loading is not likely to give rise to the potential required for an incendive spark.

Experiments on water washing in tanks up to 2500 m^3 gave a maximum potential of 7.9 kV except for certain esters. There are, however, certain features which would tend to increase the safety factor. One is that the potential was measured in the middle of the earth free volume, but an earthed probe is unlikely to exist at this point. Moreover, chemical tankers use washing machines which do not produce large slugs of water and probably in these conditions the potential required for an incendive spark exceeds 15 kV. It is concluded that in water washing also the potential required for an incendive spark is unlikely to occur.

The potential obtained in water washing for ethyl acetate, however, was 11.7 kV and that for methyl acrylate was also higher. These esters are therefore special cases.

The steam cleaning experiments gave a maximum potential of 18 kV in a 1200 m^3 tank. It is concluded that in this case an incendive spark could, in principle, occur. However, steam cleaning is used only after water washing so that a flammable atmosphere should not be present.

Further work on this topic is described by Jones and Bond, who define a tank centre space potential (TCSP) as the criterion to be considered. They develop a model to estimate the hazard threshold value of this potential. The model does not, however, predict the actual value of the potential which will occur in a given situation; this must be obtained by other means. They also give information on incidents and incident rates for cargo tank fires and explosions on chemical tankers, as described below.

23.15.3 Inert gas systems

One of the principal means of preventing fire on ships carrying flammable materials is the use of inerting. Inerting is treated in *Inert Gas Systems* (IMO, 1990 IMO-860) and by Rushbrook (1979), Gebhardt (1980), Berkel (1982), R.K. Roberts (1983), Anon. (1984r), Anon. (1984s) and Oellrich (1987).

An account of the methods available for generating an inert gas, usually nitrogen, and of its applications has been given by Oellrich (1987), who lists the following methods of generation:

(1) combustion processes;
(2) catalytic combustion of ammonia;
(3) pressure swing adsorption;
(4) permeation processes;
(5) cryogenerators;
(6) boiler flue gas.

These processes differ in various respects, including the required oxygen purity, energy consumption, convenient plant size and economics.

Some basic requirements of a nitrogen generation process are high purity oxygen, preferably $< 0.3\%$, high capacity and low space requirements.

There are several functions for which inert gas may be required. They include:

(1) gas freeing;
(2) inerting prior to loading;
(3) purging and padding.

Gas freeing is the purging of a tank with inert gas prior to purging with air for tank inspection. Purging and padding is carried out to render the gas space above the cargo in the tank inert and to keep it so.

Inerting is typically used to reduce the oxygen content of the space inerted to below 5%.

There are certain problems and hazards associated with the use of inerting. These include:

(1) contamination of cargo;
(2) overpressure of tank;
(3) neutralization of inhibitors;
(4) asphyxiation of crew.

The use of inert gas such as boiler flue gas may contaminate the chemicals carried. The inerting operations may cause overpressure of the tank. Certain inhibitors used to prevent polymerization of monomers may be rendered ineffective unless there is sufficient oxygen in the atmosphere. An example is hydroquinone which is used as an inhibitor in vinyl acetate. The large quantities of inert gas required present a hazard of asphyxiation to the crew.

The IMO requirements for inerting are given in *Inert Gas Systems* (IMO, 1990 IMO-860), which covers oil tankers, product carriers and combination carriers and also deals with chemical tankers. As already described, there are also inerting requirements in the *IGC Code* and the *IBC Code*.

The use of inerting is an accepted practice for oil tankers, but has been controversial for chemical tankers. For oil tankers the provision of an inert gas system has become mandatory. Under SOLAS 1974 it is required for tankers $>100\,000$ DWT and under SOLAS 1978 for existing tankers $>40\,000$ DWT, and new tankers $>20\,000$ DWT.

The IMO has also considered a proposal for a requirement for chemical tankers, but there are certain problems and the proposal has been resisted. The problem has been discussed by H.R. Edwards (1983). Difficulties in the use of inert gas on chemical tankers are the facts that the most common method of inerting, i.e, the use of inert gas from oil firing, is liable to contaminate the cargo and that inhibition of polymerization of monomers is less effective due to lack of oxygen. Given these difficulties, the relatively low number of incidents and the appreciable costs, it is argued that inerting is not justified.

The work by M.R.O. Jones and Bond (1984, 1985) on static electricity and on fires and explosions in chemical tankers may be regarded as a contribution to assessing the risks from these latter hazards. A study by Lloyd's Register showed that for chemical tankers the use of inerting would lead to only a marginal reduction in the frequency of fire but an appreciable increase in the frequency of tank entry incidents (Anon., 1984s).

The IMO requirements for environmental control, or control of the atmosphere in the vapour space of the cargo tanks, are given in Chapter 9 of the *IBC Code*. This states that vapour spaces 'may require to have specially controlled atmospheres' and describes four methods, of which inerting is one.

23.16 Marine Transport: Liquefied Flammable Gas

23.16.1 Regulatory controls and codes

The controls and codes for ships carrying hazardous materials have already been described. For gas carriers transporting liquefied flammable gas (LFG) the *IGC Code* is of particular relevance.

23.16.2 Hazard scenarios

Principal hazards from gas carriers are spillage of a large quantity of LFG onto water, as a result of grounding, collision or leak during transfer, and a large fire or explosion on the ship, particularly in or near a port.

23.16.3 Ship design and operation

The design of liquefied gas carriers is described in the *IGC Code* and in *Liquefied Gas Handling Principles on Ships and in Terminals* (SIGTTO, 1986/3). As stated earlier, gas carriers are designed with cargo tanks integral with the vessel or with separate tanks. Plate 29 shows a typical gas carrier, in this case one with separate spherical tanks.

Gas carriers fall into six groups: (1) fully pressurized carriers, (2) semi-refrigerated/semi-pressurized carriers, (3) semi-pressurized/fully refrigerated carriers, (4) fully refrigerated LPG carriers, (5) ethylene carriers and (6) LNG carriers. The first three groups are most suitable for smaller cargoes and the fourth for larger cargoes of LPG or ammonia.

The principal contents of the *IGC Code* are shown in Table 23.32, Section A, and illustrate many of the most important features of gas carriers.

The code specifies degrees of damage and flooding which the ship itself should be designed to survive.

The *Code* recognizes five types of cargo containment system: (1) independent tanks, (2) membrane tanks, (3) semi-membrane tanks, (4) integral tanks and (5) internal insulation tanks. Independent tanks are classified as Type A, B or C. Type A tanks are basically constructed of plane surface. Type B tanks may be constructed of plane surface or as pressure vessels. For a Type B tank the stress analysis is more comprehensive than that for a Type A tank. Type C tanks are normally cylindrical or spherical pressure vessels. Figures 23.11(a)–(c) illustrate these three types. Figures 23.11(d) and 23.11(e) show two principal membrane systems, those of Gaz Transport and Technigaz.

The *Code* gives requirements for the pressure system, including cargo and process piping, type tests on piping components, piping fabrication and jointing details, testing of piping, cargo system valves, cargo hoses, cargo transfer methods and vapour return connections. It requires remotely operated emergency shut-down valves on each cargo hose connection, operable from at least two points on the ship.

The *IGC Code* contains a number of requirements for materials of construction, specifying a range of steels for successively lower minimum design temperatures down to -165°C, and for welding and non-destructive testing.

Table 23.32 *Principal contents of the IGC Code and the IBC Code (International Maritime Organization, 1983 IMO-782 and 1990 IMO-100)*

A IGC Code 1983

Chapter No.	
1	General
2	Ship survival capability and location of cargo tanks
3	Ship arrangements
4	Cargo containment
5	Process pressure vessels and liquid, vapour and pressure piping systems
6	Materials of construction
7	Cargo pressure/temperature control
8	Cargo tank vent systems
9	Environmental control
10	Electrical installations
11	Fire protection and fire extinction
12	Mechanical ventilation in the cargo area
13	Instrumentation (gauging, gas detection)
14	Personnel protection
15	Filling limits for cargo tanks
16	Use of cargo as fuel
17	Special requirements
18	Operating requirements
19	Summary of minimum requirements

B IBC Code 1986

Chapter No.	
1–4	Titles essentially as *IGC Code*
5	Cargo transfer
6–14	Titles essentially as *IGC Code*
15	Special requirements
16	Operational requirements
16A	Additional measures for the protection of the marine environment
17	Summary of minimum requirements
18	List of chemicals to which the code does not apply
19	Requirements for ships engaged in the incineration at sea of liquid chemical waste

The *Code* gives detailed requirements for cargo tank venting, both pressure relief and vacuum relief, including settings and capacities. The pressure relief valve capacity should be able to handle the maximum capacity of the cargo tank inerting system or the fire exposure, whichever is the greater. There is also a requirement for an additional pressure relieving system for liquid level control. The *Code* gives the formulae for valve sizing.

Under the heading of environmental control the code contains requirements for the gas freeing of cargo tanks, including for flammable gases the use of inert gas. There are also requirements for environmental control in the hold spaces for cargo containment systems other than Type C independent tanks and for the spaces surrounding tanks of this latter type.

In respect of fire protection, ships carrying products which are flammable or toxic are required by the *IGC Code* to have a water spray system for cooling, fire prevention and crew protection, and those carrying flammables are required to have dry powder systems. The *Code* specifies the areas and features to be protected by each system and gives equipment capacities and application rates.

Matters covered under the special requirements of the *Code* are: (1) materials of construction; (2) independent tanks; (3) refrigeration systems; (4) deck cargo piping; (5) exclusion of air from vapour spaces; (6) moisture control; (7) inhibition; (8) permanently installed toxic gas detectors; (9) flame screens on vent outlets; (10) the maximum allowable quantity of cargo per tank; (11) submerged electric cargo pumps; and (12) various chemicals, including chlorine, ammonia, ethylene oxide, propylene oxide/ethylene oxide mixtures and vinyl chloride.

The code gives a tabular summary of minimum requirements, covering (a) product name, (b) United Nations (UN) number, (c) ship type, (d) independent Type C tank, (e) control of vapour space in cargo tanks, (f) vapour detection, (g) gauging, and (h) special requirements.

One of the principal liquefied gases carried is LNG. Some features of LNG carrier design include (1) cargo tank design, (2) cargo protection, (3) cargo tank cooling, (4) cargo tank insulation, (5) boil-off, (6) reliquefaction and (7) propulsion.

For LNG carriers there are three principal cargo tank designs in use. These are the Gaz Transport (GT) membrane, the Technigaz (TGZ) membrane and the Moss Rosenberg spherical tank. The three types have been described by Bouckaert and Cappoen (1984). An account of the GT design has been given by Jean and Bourgeois (1985) and of the Technigaz design by Ogawa *et al.* (1986).

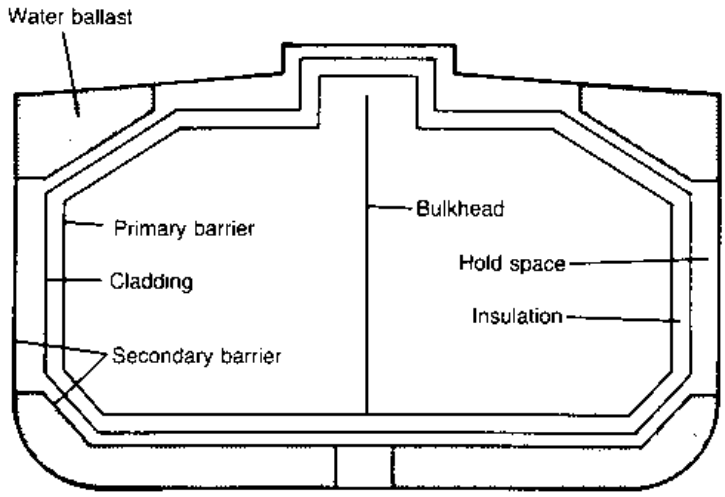
Protection of the cargo tanks against grounding and collision is an important aspect of the tank design. Designs based on independent tanks have obvious advantages here, but membrane design has also given good protection in practice.

Since the LNG carried is very cold, it is necessary to ensure that its loading does not create a hazard due to thermal shock. The empty tanks may be sprayed with LNG before loading to cool them down or the tanks may be kept permanently cool. In the GT system the solution adopted is the use of invar as the membrane material.

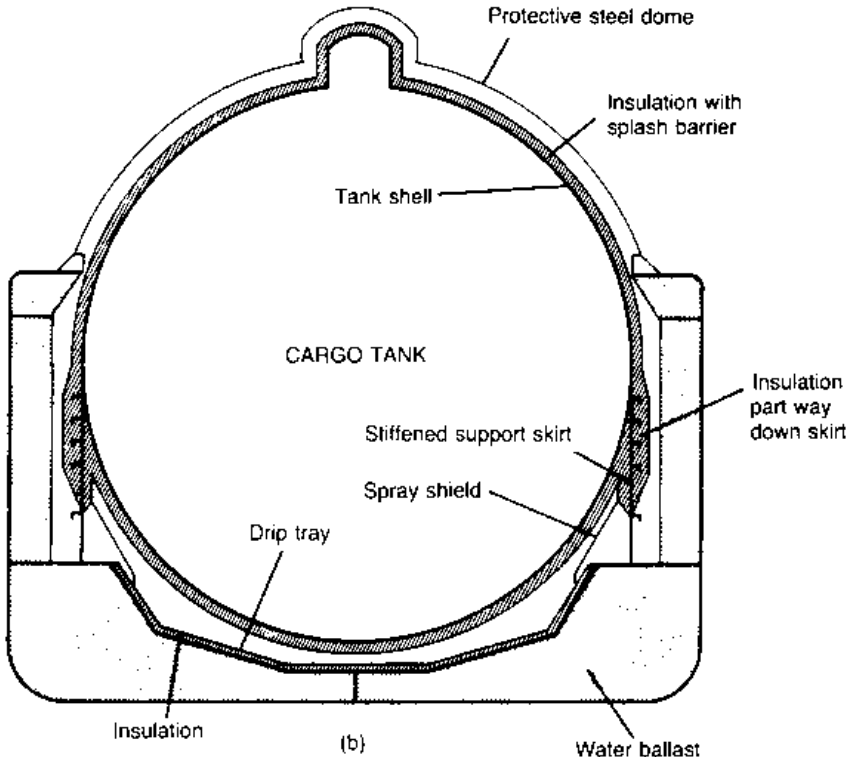
There must also be good thermal insulation. There are a number of different insulation systems in use. Accounts are given by Bouckaert and Cappoen (1984) and Böckenhauer (1987). The effectiveness of the insulation is such that the boil-off rate achieved is very low. The boil-off may be used as fuel for the ship's boilers. Alternatively, a reliquefaction system may be provided.

There is a trend towards the use of diesel engines as the propulsion system. Accounts have been given by Engesser *et al.* (1987), Grone and Pedersen (1987) and Terashima *et al.* (1987).

LPG carriers are often designed as flexible carriers able to handle not only LPG but also other liquefied gases. A typical cargo list for such carriers was given in Section 23.12. The design of flexible semi-refrigerated carriers has been described by Faridany and Ffooks

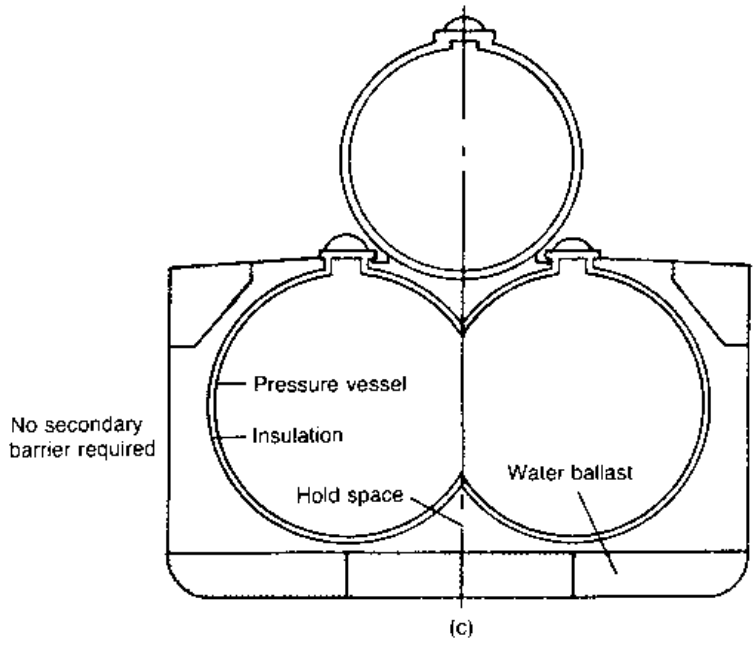


(a)

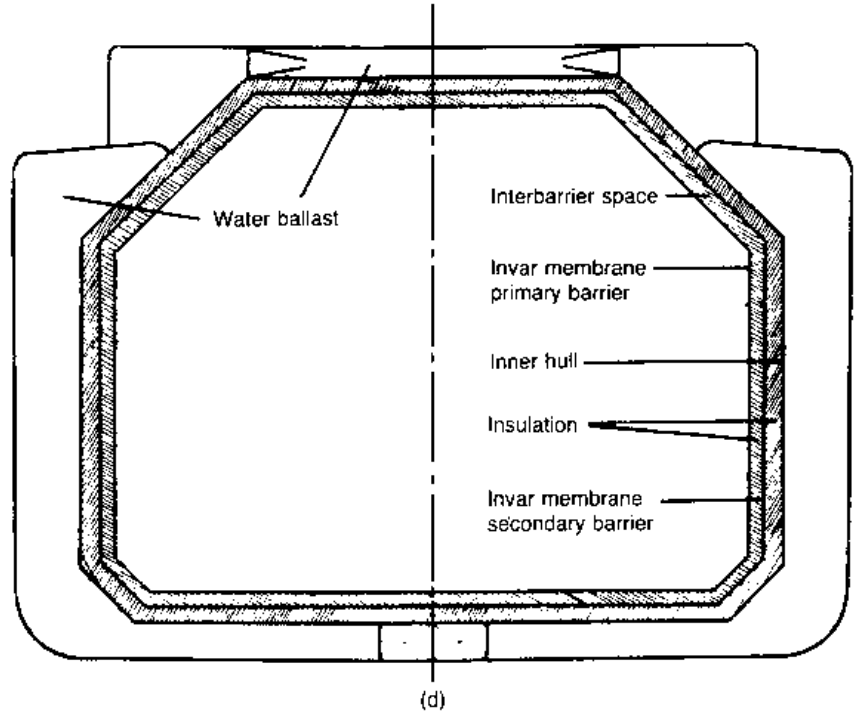


(b)

Figure 23.11 *Liquefied gas carrier cargo containment systems (Society of International Gas Tanker and Terminal Operators, 1986/6; reproduced by permission): (a) Type A prismatic self-supporting tank for fully refrigerated gas; (b) Type B spherical self-supporting tank; (c) Type C tank for semi-pressurized/fully refrigerated gas; (d) Gaz Transport membrane containment system for LNG; (e) Technigaz membrane barrier and insulation system for LNG*



(c)



(d)

Figure 23.11 *continued*

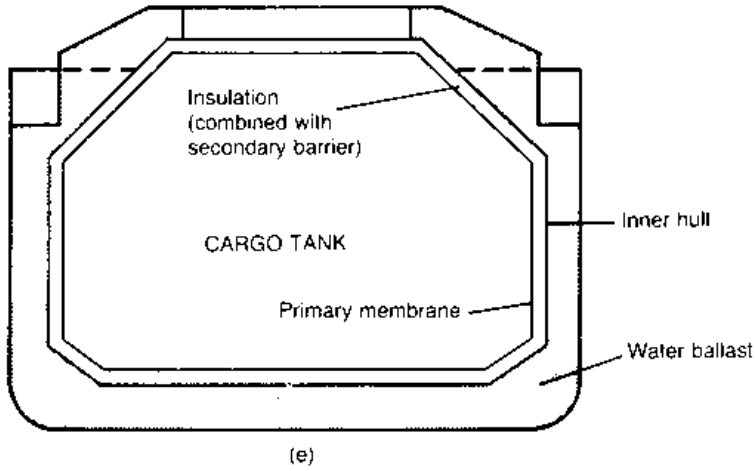


Figure 23.11 *continued*

Table 23.33 *Some LFG terminals*

A LNG	
Location	*Reference(s)*
Antwerp, Belgium	McKinney and Oerlemans (1985)
Arzew, Algeria	Filstead (1965); Pierot (1968); Rerolle (1968); Laur (1970); Bourguet (1972); Seurat, Hostache and Gros (1978); Benazzouz and Abbou (1987)
Brunei	C. Gibson (1973); Jenkins, Frieseman and Prew (1974); Ploum (1977)
Canvey, UK	Ward and Hildrew (1968a-b); Eke, Graham and Malyn (1974)
Cove Point	Kime, Boylston and van Dyke (1980)
Fos-sur-Mer, France	Asselineau *et al.* (1972); Leray, Petit and Paradowski (1986a,b)
Kenai, Alaska	Horn *et al.* (1974)
Memphis	Stanfill (1968)
Montoir-de-Bretagne, France	Colonna, Lecomte and Caudron (1986)
Skikda, Algeria:	Dolle and Gilbourne (1976); Khenat and Hasni (1977)
Floating terminal	Anspach, Baseler and Glasfeld (1979)
Offshore terminal	Rust and Gratton (1980)
B LPG	
Location	*Reference(s)*
Port Bonython, Australia	Craker, Scott and Dutton (1986)
Offshore terminal	Chauvin and Bonjour (1985); Branchereau and Bonjour (1986)
C NGL	
Location	*Reference(s)*
Mossmorran	Sellers, Luck and Pantony (1985)

(1983) and by Backhaus and Olschlager (1985), the first being for an LPG carrier with multi-lobe tanks and the second an ethylene carrier with tri-lobe tanks.

With respect to operation, Chapter 18 of the *IGC Code* treats the following topics: (1) cargo information, (2) compatibility, (3) personnel training, (4) entry into spaces, (5) low temperature cargoes, (6) protective equipment, (7) systems and controls, and (8) cargo transfer.

23.16.4 Terminal design and operation

A terminal for liquefied flammable gas is either an export or an import terminal and normally handles mainly either

LPG or LNG. Some principal LFG terminals are listed in Table 23.33.

An account of LPG terminals in Europe has been given by de Sola (1985). Some principal export terminals are those at Sullom Voe (Shetlands), Flotta (Orkneys), St Fergus-Mossmorran, Grangemouth, Teesside (UK) and at Kaarstoe (Norway). Some principal import terminals are those at Canvey and Killingholme (UK), Rotterdam, Terneuzen and Flushing (Netherlands), Antwerp (Belgium) and Lavera (France).

The LPG terminal at Mossmorran has been described by Sellers, Luck and Pantony (1985). An account of the LNG terminal at Arzew, Algeria, has been given by Benazzouz and Abbou (1987). The authors give a description of the first 20 years of operation of the site. This includes a detailed listing of the principal failures and associated downtime.

Terminals differ depending on whether they are import or export terminals. An account of the differences for LNG has been given by R.A. Cox, Comer *et al.* (1980). The main elements of an import terminal are:

(1) berth for LNG ships and handling facilities;
(2) LNG storage tanks;
(3) pressure control system for tanks;
(4) gas separation and dispatch system.

The main elements of an export terminal are

(1) gas liquefaction and fractionation units;
(2) LPG storage facilities;
(3) LNG storage tanks;
(4) berth for LNG ships and handling facilities;

and sometimes

(5) slugcatcher.

These differences affect the hazards of the terminal.

23.17 Marine Transport: Chemicals

23.17.1 Regulatory controls and codes

The controls and codes for ships carrying hazardous materials have already been described. For chemical tankers the *IBC Code* is of particular relevance.

23.17.2 Hazard scenarios

Chemical tankers tend to present different hazards from those of gas carriers. These hazards include those of a runaway reaction, an explosion, a toxic release and severe pollution.

23.17.3 Ship design and operation

It is convenient at this point to consider chemical tankers, or tank ships, which increasingly have come to share common features with gas carriers. Thus, as shown in Table 23.32, Section B, the headings of the *IBC Code* are very similar to those of the *ICG Code*.

Cargo containment systems are of four types: (1) independent tank, (2) integral tank, (3) gravity tank, and (4) pressure tank.

The cargo tank vent system is either an open vent or a controlled venting system using pressure/vacuum valves. The code gives requirements on the type of system for each product.

The *IBC Code* recognizes four types of environmental control system: inerting, padding, drying and ventilation. It gives requirements on the type of system for each product.

Matters covered under the special requirements of the *Code* include requirements concerning (1) acids, (2) toxic products, (3) inhibited cargoes, (4) high vapour pressure cargoes, (5) cargoes with a wide flammable range and low ignition temperature and (6) cargo contamination, together with requirements for a number of specific chemicals.

The *Code* gives a tabular summary of minimum requirements covering (a) product name, (b) UN number, (c) pollution category, (d) hazards, (e) ship type, (f) tank type, (g) tank vents, (h) tank environmental control, (i) electrical equipment, (j) gauging, (k) vapour detection, (l) fire protection, (m) materials of construction, (n) respiratory and eye protection and (o) special requirements.

With respect to operation, Chapter 16 of the *IBC Code* treats the following topics: (1) tank filling, (2) cargo information, (3) personnel training, (4) opening of and entry into tanks, (5) stowage of cargo samples and (6) cargoes not to be exposed to excessive heat.

There are an appreciable number of chemicals to which the code does not apply, and these are listed in it.

23.18 Marine Transport Environment

23.18.1 Shipping

Information on the number of ships is available through Lloyds Register. The world fleet of oil tankers, chemical tankers and liquefied gas carriers as given by Lloyds for 1986, quoted by Sanders and Aldwinckle (1987), is:

Ship type	*No. of ships*	*Deadweight tonnage* ($\times 10^6$ te)
Oil tanker	5985	240.2
Oil/chemical tanker	502	7.3
Chemical tanker	861	6.1
Gas carrier	770	10.1
Total	8133	263.7
World fleet	75266	647.6

Further information on liquefied gas carriers (LGCs) is given in Section 23.16.

23.18.2 Marine incidents

Lloyds Register also provides information on shipping incident statistics. Other sources of information are the *Interim Report of the Tanker Safety Group* (Tanker Safety Group, 1977) and *Analysis of Serious Casualties to Sea-Going Tankers* 1968–80 by the IMO.

Table 23.34 gives data from the Tanker Safety Group report. The accident rates are similar for all classes of ship. There is no evidence that very large ships, particularly very large crude carriers (VLCCs) are more liable to accidents. The yearly figures show no discernible trend with time.

Table 23.34 *Serious casualties to and cargo fires/explosions on tankers carrying oil and chemicals during the period 1968–75 (Tanker Safety Group, 1977) (Courtesy of Trade and Industry)*

A Serious casualties[a]

Year	*Tanker size (dwt)*					
	10 000 to < 150 000			> 150 000		
	No. of ships	*No. of serious casualties*	*Serious casualty rate per tanker per year*	*No. of ships*	*No. of serious casualties*	*Serious casualty rate per tanker per year*
1968	2 927	79	0.027 0	16	0	–
1969	2 934	72	0.024 5	57	4	0.0702
1970	2 928	57	0.019 4	121	3	0.024 8
1971	2 956	56	0.018 9	198	8	0.040 4
1972	2 950	67	0.022 7	267	7	0.026 2
1973	2 930	63	0.021 5	351	2	0.057 0
1974	2 988	64	0.021 4	455	5	0.011 0
1975	2 971	78	0.026 3	582	10	0.017 2
Total	23 584	536	0.022 7	2 047	39	0.019

B Fires

Year	*Tanker size (dwt)*			
	10 000 to < 150 000		*≥ 150 000*	
	No. of cargo fires/ explosions	*Cargo fire/ explosion rate per tanker per year*	*No. of cargo fires/ explosions*	*Cargo fire/ explosion rate per tanker per year*
1968	13	0.004 4	0	–
1969	9	0.003 1	3	0.005 26
1970	9	0.003 1	0	–
1971	7	0.002 4	1	0.005 1
1972	19	0.006 4	2	0.007 5
1973	9	0.003 1	2	0.005 7
1974	10	0.003 3	0	–
1975	5	0.001 7	0	–
Total	81	0.003 4	8	0.003 9

[a] Serious casualties are those involving loss of life, structural damage or pollution.

For chemical tankers, information on fires and explosions has been given by M.R.O. Jones and Bond (1984), as shown in Table 23.35 which gives the number of fires and explosions, the size of vessel involved, the operation involved in each case and the source of ignition.

23.18.3 Substandard vessels

A study of the relation between the standards of ship design and operation and the probability of a ship accident has been reported in *Substandard Tankers* (van Poelgeest, 1978). In a comparison between 37 tankers owned by a Greek tanker operator and 37 oil company-owned tankers for the year 1973, this author found that whereas the latter ships were involved in some 10 incidents, mostly relatively minor, with a loss of 10 vessel-days, 28 of the former were involved in accidents, in many cases sustaining serious damage, and some in more than one incident, with a loss of 1072 vessel-days. The total of substandard tankers in the world tanker fleet of vessels of 6000 GRT and larger is estimated by van Poelgeest as approximately 450 vessels or 13–15% of the fleet.

Further information on substandard vessels is available in the 1993 *Annual Report* of the Paris Memorandum (1993). This gives statistics on the number of vessels, the number delayed/detained following inspection and the major categories of deficiency. In 1993 the there were 17 294 inspections covering 112 523 ships, with 43 071 deficiencies and 926 detentions. The average proportion of vessels detained is about 8%, with some 10 states having at least double this proportion. The proportions for France, Germany, the UK and the USA are 4%, 3%, 2% and 0%, respectively. The proportion of the total delays/detentions attributable to different types of

Table 23.35 *Fire and explosions on chemical tankers in the period 1973–83 (after M.R.O. Jones and Bond, 1984)*

A Number of incidents

Location	*No. incidents*
Cargo tank	14
Pump room	9
Engine room	34
Other	11
Total	68

B Cargo tank incidents: vessel size

Vessel size (DWT)	*No. incidents*
< 1000	7
1000–9999	2
10 000–19 999	2
> 20 000	3
Total	14

C Cargo tank incidents: operations involved

Operation	*No. incidents*
Loading	2
Steaming out tank	2
Water washing with rubber hose and wooden nozzle	1
Inspection/cleaning by persons inside tank	3
Handling of slops	3
Polymerization of product	1
Overpressurization of tank with nitrogen	1
'While being pushed by a tug'	1
Total	14

D Cargo tank incidents: source of ignition

Ignition source	*No. incidents*
Static electricity (attributed or probable)	5
Frictional spark	1
Light bulb	2
Flare stack	2
Unknown	2
No ignition[a]	2
Total	14

[a] Of these two incidents classed as fire/explosion, one was a case where the tank was overpressurized by nitrogen, and the other was a case where polymerization of acrylic acid occurred, causing a high temperature but no fire or explosion.

vessel includes 1.3% for gas carriers, 5.3% for chemical carriers and 10.7% for tanker/combination carriers, the proportions of each of these types detained being 6%, 8% and 7%, respectively. The breakdown of the major categories of deficiency is: life saving appliances, 24.3%; fire fighting appliances, 16.8%; general safety, 12.9%; navigational equipment, 11.6%; ship's certificates, 5.2%; MARPOL requirements, 4.7%; and other, 24.6%. The report refers to the 'increasingly ageing world fleet operating in a marginal market'.

23.18.4 Shipping: LFG

There is a large trade world-wide in liquefied flammable gases (LFGs). Accounts of this trade are given in *LNG Log* by SIGTTO (1986) and by Aprea (1983), Boukaert and Cappoen (1984) and Glass (1987).

LNG Log contains statistical information on individual LNG carriers and terminals; on cargo containment systems; and on carrier movements, or voyages. In 1986 there were 963 movements of LNG carriers.

Further data on the number of LNG and LPG carriers are provided by Aprea (1983), Blything and Edmondson (1983), Bouckaert and Cappoen (1984) and Aldwinckle and Mclean (1985). Tables 23.36 and 23.37 give data on the world LNG and LPG fleets, respectively.

The number of LNG carriers (*c.* 1984) is given in Table 23.36, Section B, as 81. A vessel capacity of 125 000 m^3 has become the standard size for a modern LNG carrier. For LPG carriers the number (*c.* 1984) given in Table 23.37, Section B is 708. Of these 213 were > 5000 m^3 capacity.

Only a proportion of the LPG fleet consists of refrigerated carriers, the rest being pressure carriers. Holdsworth (1985) states that a figure of 107 ships represents 44% of world capacity in refrigerated LPG ships, which suggests a world fleet of some 243 vessels.

The approximate world-wide deep sea movements per year of LFGs other than LNG and LPG are given by Glass (1987) as 370 for ethylene, 290 for propylene and 520 for butadiene.

23.18.5 Marine incidents: LFG

Incident statistics for LNG carriers are given by R.A. Cox, Comer *et al.* (1980) and Aldwinckle and McLean (1985), while Blything and Edmonson (1983) give data on fires and explosions. For LPG carriers data on incident statistics are given by Aldwinckle and McLean (1985) and data on fire and explosion are given by Blything and Edmondson (1983).

Table 23.38 gives incident data for the world LNG and LPG fleets and, for comparison, for the world cargo fleet. These include incidents involving fire and explosion as well as grounding and collision. Further data on LNG carrier incidents is given in Table 23.39, which again provides information both on grounding and collision and on fire and explosion. Data on LPG carrier fire and explosion are shown in Table 23.40 and data an stranding and collision are given in Table 23.41. For the world LGC fleet, which includes both LNG and LPG carriers, data are given in Table 23.42.

These overall data on incidents and incident rates may be supplemented by data for specific waterways and ports. Incident data for the port of Rotterdam have been given by Ligthart. Figure 23.12 gives information on collision and stranding determined for this port.

For the Thames estuary, accident data are given in the two *Canvey Reports* as described in Appendix 7.

23.18.6 Ship collision

Two principal ship accident modes which may give rise to large loss of containment are collision and grounding.

Table 23.36 *World LNG fleet*

A Blything and Edmondson (1983) – Date: 1981

Ship capacity (m^3)	*No. of ships*
< 5000	7
> 5000	64
Total	71

B Aldwinckle and McLean (1985): No. of ships

Ship capacity (m^3)	*Ship age (year)*					
	0–4	*5–9*	*10–14*	*15–19*	*20–24*	*Total*
< 5000	1	1	8	1		11
5000–9 999	1					1
10 000–29 999		1	1	1	2	5
30 000–49 999		2	5	1		8
50 000–69 999			1			1
70 000–99 999		3	6	2		11
100 000–129 999	10	26				36
> 130 000	7	1				8
Total	19	34	21	5	2	81

Table 23.37 *World LPG fleet*

A Blything and Edmondson (1983)—Date: 1981

Ship capacity (m^3)	*No. of ships*
< 5000	409
> 5000	159
Total	568

B Aldwinckle and McLean (1985): No. of ships

Ship capacity (m^3)	*Ship age (year)*							
	0–4	*5–9*	*10–14*	*15–19*	*20–24*	*25–29*	*≥30*	*Total*
Unknown	6	3	1				2	12
< 5000	93	97	92	121	49	18	13	483
5000–9999	30	17	4	7	1			59
10 000–29 999	14	17	7	20	5		2	65
30 000–49 999	3	2	3	3	1	1		13
50 000–69 999	5	8	9	1				23
70 000–99 999	14	27	8	1				50
100 000–129 999		1	2					3
Total	165	172	126	153	56	19	17	708

Both have been the subject of study. Studies of collision include those of Minorsky (1959), Kinkead (1978 SRD R91, 1980), Böckenhauer (1980) and F.S. Harris (1986).

The requirements for collision resistance are given by Harris as stability after collision, avoidance of spillage and energy absorption by the structure.

Minorsky presented a model of collision damage based on the equations for conservation of energy and momentum. These are respectively

$$\tfrac{1}{2}m_1v_1^2 = \tfrac{1}{2}(m_1 + m_2)V^2 + E \qquad [23.18.1]$$

and

$$V = \frac{v_1 m_1}{m_1 + m_2} \qquad [23.18.2]$$

where E is the energy absorbed in the collision, m_1 is the effective mass of the striking ship, m_2 is the effective mass of the struck ship, v_1 is the speed of the striking

Table 23.38 *World LNG, LPG and cargo fleet incident frequency (incidents/1000 ship-years) (after Aldwinckle and McLean, 1985) (Courtesy of Gastech)*

		Ship type			
Casualty type[a]		*LNG carriers*	*LPG carriers*	*Total gas carriers*	*Dry cargo ships*
Collision	A	0	0.36	0.32	0.82
	B	0	1.08	0.95	5.82
	C	0	1.43	1.27	6.64
	D	0	0	0	2.97
Contact	A	0	0	0	0.21
	B	0	0.36	0.32	1.88
	C	0	0.36	0.32	2.08
	D	0	0	0	0.23
Fire/explosion	A	0	0.72	0.63	1.82
	B	0	3.58	3.16	3.37
	C	0	4.30	3.79	5.20
	D	0	2.87	2.53	4.98
Foundering	A	0	1.43	1.26	2.61
	B	0	0.36	0.32	0.33
	C	0	1.79	1.58	2.94
	D	0	0	0	8.35
Hull/machinery damage	A	0	0	0	0.29
	B	2.65	9.32	8.52	8.08
	C	2.65	9.32	8.52	8.36
	D	0	0	0	0.27
Miscellaneous	A	0	0	0	0.02
	B	0	0	0	0.22
	C	0	0	0	0.25
	D	0	0	0	0
Missing	A	0	0	0	0.15
	B	0	0	0	0.01
	C	0	0	0	0.16
	D	0	0	0	3.73
War loss/ hostility	A	0	0	0	0.25
	B	0	0	0	0.62
	C	0	0	0	0.88
	D	0	0	0	1.03
Wrecked/ stranded	A	0	1.79	1.58	2.81
	B	10.59	2.51	3.47	7.38
	C	10.59	4.30	5.05	10.19
	D	0	0	0	1.20
Total	A	0	4.30	3.79	8.98
	B	13.24	17.20	16.73	27.71
	C	13.24	21.50	20.52	36.69
	D	0	2.87	2.53	22.76

[a] A, No. of reported losses; B, No. of reported serious casualties; C = A + B; D, No. of people killed or missing. All per 1000 ship-years.

ship before collision and V is the residual speed of the two ships after the collision.

Minorsky took the effective mass of the struck ship as the actual mass plus the added hydrodynamic mass δm, which he estimated as $0.4m_2$.

He defined a resistance factor R_T as

$$R_T = \Sigma P_N L_N t_N + \Sigma P_n L_n t_n \qquad [23.18.3]$$

where L is the length of damage, P is the depth of damage and t is the thickness, and the subscripts N and n refer to the Nth member in the striking ship and the nth member in the struck ship.

Table 23.39 *World LNG carrier fleet incidents*

A General incidents (R.A. Cox, Comer et al., 1980) – Period: 1964–77

Incident type	*No. of incidents*	*Incident frequency* (incidents/1000 movements)		
		LNG traffic	*UK port survey*	
			Open sea port	*Estuarial port*
Grounding, stranding, drifting	3	0.45	0.17	0.16
Collision, impact, ramming	4	0.6	1.22	0.17
Leaks from tanks or during transfer	6	0.9	–	–
Other	6	0.9	–	–

B Fire and explosions (Blything and Edmondson, 1983) – Period: 1971–81

Ship capacity (m^3)	*No. of ship-years*	*No. of incidents*
$< 100\,000$	305	2
$> 100\,000$	145	2
Total	450	4

Table 23.40 *World LPG carrier fire and explosions (after Blything and Edmondson, 1983) (Courtesy of the Institution of Chemical Engineers)*

A Incidents per year

Ship capacity (m^3)	*No. of incidents*	*No. of ship-years*	*Incident frequency* (incidents/ship-year)
< 5000[a]	14	1850	7.6×10^{-3}
> 5000[b]	8	662	1.2×10^{-2}

B Incidents per voyage

Ship capacity (m^3)	*No. of incidents*	*No. of voyages*	*Incident frequency* (incidents/voyage)
< 5000[a]	14	14 854	8.4×10^{-4}
> 5000[b]	18	6 259	2.9×10^{-3}

C Ship area and marine location[b]

Ship area	*Ship capacity* (m^3)	*No. of incidents*		
		At sea	*In port or restricted waters*	*Total*
Engine room	< 5000	4	2	18
	> 5000	9	3	
Cargo pumps/ compressors	< 5000	–	2	4
	> 5000	–	2	
Cabins/galley	< 5000	2	–	3
	> 5000	–	1	
Other	< 5000	–	–	1
	> 5000	–	1	
Unknown	< 5000	2	2	6
	> 5000	1	1	

[a] Over period 1977–81.
[b] Over period 1971–81.

Table 23.41 *World LPG carrier groundings and collisions 1977–81 (after Blything and Edmondson, 1983) (Courtesy of the Institution of Chemical Engineers)*

Incident type	*Ship capacity* (m^3)	*No. of incidents*	*No. of ship-years*	*Incident frequency* (incidents/ship-year)
Stranding	< 5000	13	1850	7.0×10^{-3}
	> 5000	18	662	27×10^{-3}
Collision	< 5000	48	1850	2.6×10^{-2}
	> 5000	25	662	3.8×10^{-2}

Table 23.42 World LGC carrier incidents (after Aldwinckle and McLean, 1985) (Courtesy of Gastech)

Cause of damage	*Ship area*[a]																*No. of ships*
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*All*	
Collision	8					17	6				1	2	3			37	15
Grounding			1		27	1						4	1	7		41	9
Pounding					4											4	3
Ice														1		1	1
Cargo shift																	
Excess pressure	2	2	10	8		6	1						3		3	35	8
Vibration												4	7			11	4
Cargo handling							1									1	1
Wear and tear	7	1	5	5	61	24	8					4	6	10	4	135	23
Mooring													6	6		3	
Other													1		2	3	2
Contact	2	5	2		13	32						6	5	1	1	67	21
Sloshing																	
Heavy weather	6	12	12	10	23	12	6					8	3	2	3	97	20
Fire												3	1			4	1
Flooding																	
Unknown	14	6	29	16	76	70	9					16	32	34	18	320	42
All	39	26	39	59	204	162	31				1	47	62	55	37	762	48
No. of ships	17	16	21	13	33	35	13				1	20	21	22	20		48
Proportion of all areas (%)	5.1	3.4	7.7	5.1	26.8	21.3	4.1				0.1	6.2	8.1	7.2	4.9	100	
Incidence (per 100 months)	0.64	0.42	0.96	0.64	3.33	2.65	0.51				0.02	0.77	1.01	0.90	0.60	12.45	

[a] 1, Fore end structure; 2, forecastle and deck; 3, transverse bulkheads (in way of cargo space); 4, longitudinal bulkheads (in way of cargo space); 5, bottom structure (in way of cargo space); 6, side structure (in way of cargo space); 7, deck structure (upper); 8, deck structure (tween); 9, weather deck hatchways and covers; 10, tween deck hatchways and covers; 11, bridge/deck houses and decks (excluding poop and forecastle); 12, engine room (including bottom structure); 13, aft end structure (excluding engine room sternframe and rudder); 14, rudder (excluding bow); 15, miscellaneous.

From ship collision data he obtained an empirical correlation between E and R_T, as illustrated in Figure 23.13. The relation may be expressed in the form

$$E = mR_T + c \qquad [23.18.4]$$

where c and m are constants.

Minorsky also defined an absorbed energy coefficient K and a ratio R of mass of the striking and struck ships:

$$K = \frac{m_2 + \delta m}{m_1 + m_2 + \delta m} \qquad [23.18.5]$$

$$R = m_1/m_2 \qquad [23.18.6]$$

Figure 23.14 shows the relation given by Minorksy between the two parameters. As $R \to 0$, $K \to 1$, and as $R \to 0$, $K \to 0$. The relationship is not very sensitive to the value of δm. Using this model Minorsky was able to determine the critical impact speed of the striking ship required to cause a given degree of damage.

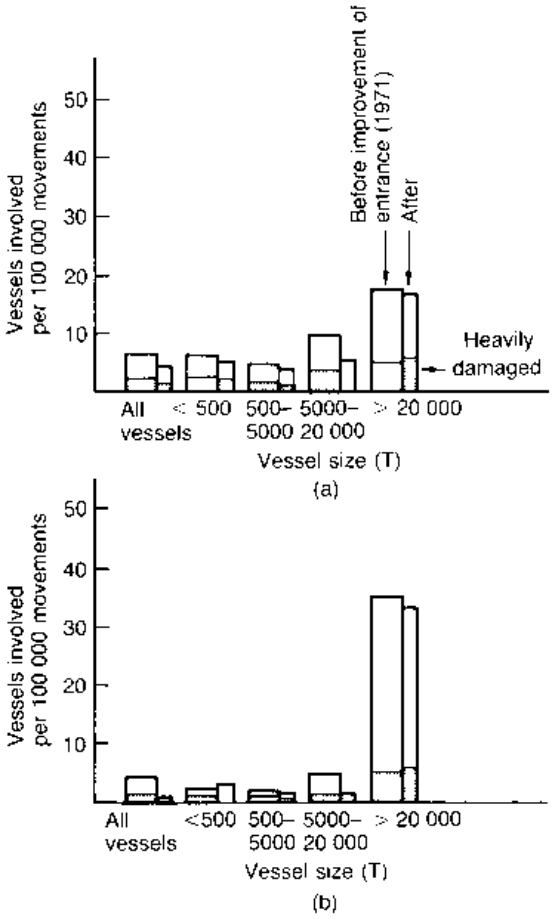


Figure 23.12 *(a) Collision ratio and (b) stranding ratio per tonnage class for vessels entering and leaving Rotterdam. T, gross registered ton (= 100 ft^3) (Ligthart, 1980) (Courtesy of Elsevier Science Publishers)*

The following treatment by Böckenhauer (1980) for collision damage to a gas carrier is typical of analyses based on the Minorsky method. From Equations 23.18.1 and 23.18.2

$$E = \frac{m_1 m_2}{2(m_1 + m_2)} v_1^2 \qquad [23.18.7]$$

Then at the critical impact speed v_{cr} of the striking ship and at the corresponding critical energy absorption E_{cr}

$$E_{cr} = \frac{m_1 m_2}{2(m_1 + m_2)} v_{cr}^2 \qquad [23.18.8]$$

or

$$v_{cr} = \left(\frac{2E_{cr}(m_1 + m_2)}{m_1 m_2}\right)^{\frac{1}{2}} \qquad [23.18.9]$$

The critical energy absorption E_{cr} is given either as the sum of the energy absorptions of the striking ship E_1, and of the struck ship E_2:

$$E_{cr} = E_1 + E_2 \qquad [23.18.10a]$$

or as

$$E_{cr} \approx 2E_2 \qquad [23.18.10b]$$

whichever is the lesser. The energy absorption E_2 is obtained from the resistance factor using an expression similar to Equation 23.18.3 but with a different definition of the resistance factor.

If the struck ship is moored at a jetty so that the residual speed V is zero

$$\tfrac{1}{2} m_1 v_1^2 = E \qquad [23.18.11]$$

$$v_{cr} = \left(\frac{2(E_{cr} + E_f)}{m_1}\right)^{\frac{1}{2}} \qquad [23.18.12]$$

where E_f is the energy absorption of the fender. This is taken as

$$E_f \leq 0.3 \qquad [23.18.13]$$

Some critical impact speeds where the struck ship is an LNG or LPG carrier as obtained by Böckenhauer are given in Table 23.43.

Kinkead (1978 SRD R91) has studied the collision of LNG carriers using a method based on that of Minorsky but extended by a more detailed analysis of the energy absorbed in the processes causing damage, which he calls the substantiation analysis.

Figure 23.15 shows Minorsky-type curves obtained in this work. The dotted line is based on the more detailed substantiation analysis. Its principal feature is that it indicates that for striking ships in the displacement range 15 000—30 000 ton the critical impact speed is considerably less than the simpler analysis suggests.

Kinkead also gives a set of curves for the critical impact speed of the striking ship hitting an LNG carrier under different conditions, as shown in Figure 23.16.

23.18.7 Ship grounding

Of at least equal importance are ship groundings. Here there are two somewhat different scenarios which need to be considered. One is where the ship is moving at speed and its bottom is torn by a rock. Treatments of this situation have been given by Kitamura, Okumoto and Shibue (1978) and by Vaughan (1978). It has been shown by Poudret *et al.* (1981) that Vaughan's approach fits well such a grounding incident which occurred with the *El Paso Paul Kayser*, as described below.

The other scenario is grounding of the ship at low speed as a result of weather, currents, loss of control, etc. This is probably the situation which is most likely to occur in confined waterways. It has been studied by Johnsen and Jensen (1983) for the case of smooth rocks and by Kinkead (1983 SRD R 342, 1983) for that of sharp rocks.

The ships considered by Kinkead are LPG carriers in the capacity range 11 754—58 950 m^3. Grounding may occur with the ship moving forwards or sideways. For the ridged rock formation considered he obtains using a Minorsky-type analysis for a 15 495 m^3 carrier for forward grounding a critical grounding velocity of 5.57 knot and for a 31 296 m^3 carrier one of 5.11 knot. The sideways critical grounding velocities for these two vessels obtained from Minorksy analysis are 3.82 and 3.23 knot, respectively. However, using a more detailed

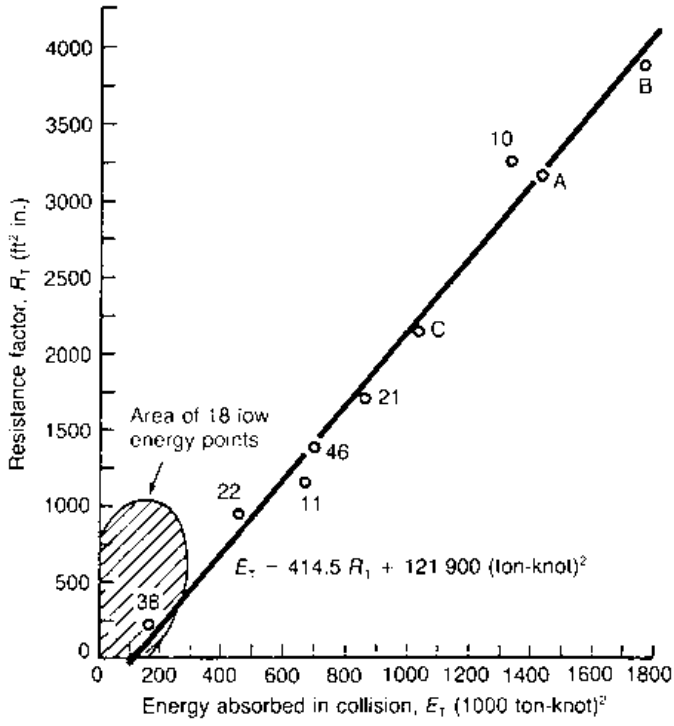


Figure 23.13 *Minorsky model of ship collision: empirical correlation between resistance to penetration and energy absorbed in collision (Minorsky, 1959) (Courtesy of the* Journal of Ship Research*)*

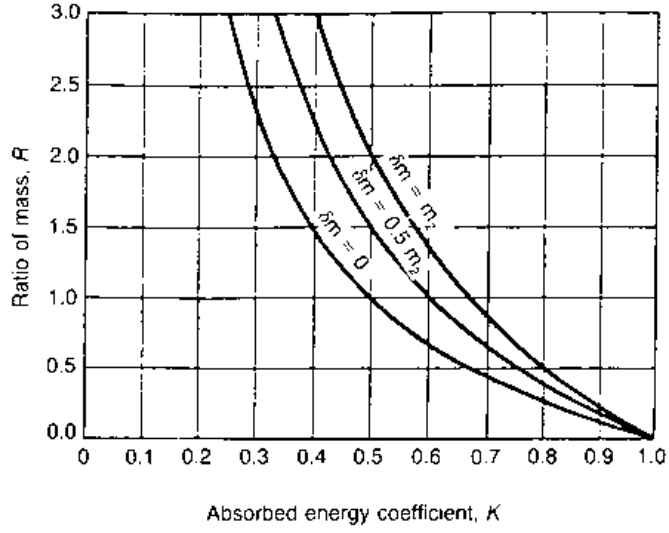


Figure 23.14 *Minorsky model of ship collision: effect of added virtual mass of water on energy absorbed in collision (Minorsky, 1959) (Courtesy of the* Journal of Ship Research*)*

Table 23.43 *Estimated critical impact speeds for ship collision for gas carriers (after Böckenhauer, 1980) (Courtesy of Gastech)*

Critical impact speed (knot)				
Struck ship	*Sister ship*	*LPG carrier (6 000 m^3)*	*Dry cargo ship*	*Oil tanker*
LPG carrier:				
6 000 m^3	–	2.6 (2.0)	2.3 (1.5)	4.5 (1.1) 3.5 (1.8)[b]
54 000 m^3	1.9 (1.5)	3.4 (3.2)	2.8 (2.5)	1.3 (0.9)[c]
LNG carrier:				
125 000 m^3, membrane	3.7 (2.8)	5.0 (4.8)	4.0 (3.8)	4.0 (2.5)
125 000 m^3, spheres	5.9 (4.5)	9.0 (8.6)	6.5 (6.1)	4.8 (3.0)

[a] Values in brackets are for struck ship moored at jetty.
[b] Oil tanker fully loaded.
[c] Oil tanker in ballast.

analysis the latter two values reduce to 2.69 and 2.86 knot, respectively. The analysis contains some conservative assumptions. One is that the rock is not friable, another that no energy is absorbed by other rock projections.

Kinkead states that imperfectly controlled manoeuvres during berthing of supply vessels at offshore platforms have occurred with sideways collision impact velocities of between 2.9 and 4.0 knot (between 1.5 and 2.0 m/s). Thus the impact velocities which occur under imperfect control are of the same order as the estimated critical grounding velocities.

23.18.18 Piracy

A quite different kind of risk is that posed by piracy. The activities of pirates are monitored by the regional piracy centre of the International Maritime Bureau in Kuala Lumpur. Most attacks have occurred in the South China Sea, off Hong Kong and around Indonesia, and also off Somalia. In 1994, 60 vessels were boarded by pirates, almost twice as many as in the previous year. In several cases ships were taken over and sailed to a port, where the cargo was unloaded and stolen. Most of the ships attacked were dry cargo vessels, but eleven oil tankers, four gas carriers and two chemical tankers were also involved.

23.19 Air Transport

Regulatory control of the carriage of hazardous materials by air has traditionally been the concern of the Restricted Articles Board of the International Air

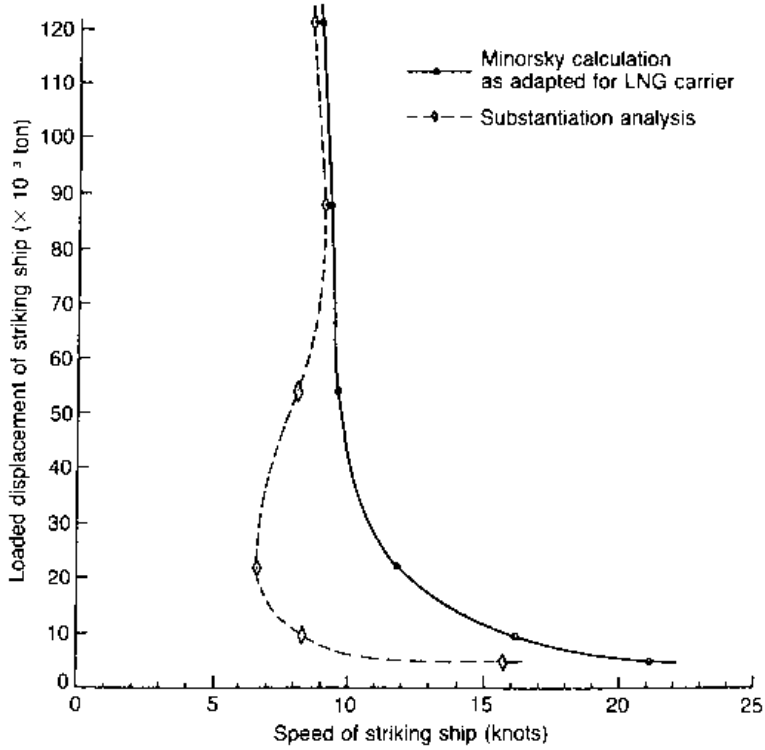


Figure 23.15 *Kinkead model of ship collision: comparison with Minorsky model for the case of a methane carrier stationary in mid-channel (Kinkead, 1978 SRD R391) (Courtesy of the UKAEA Safety and Reliability Directorate)*

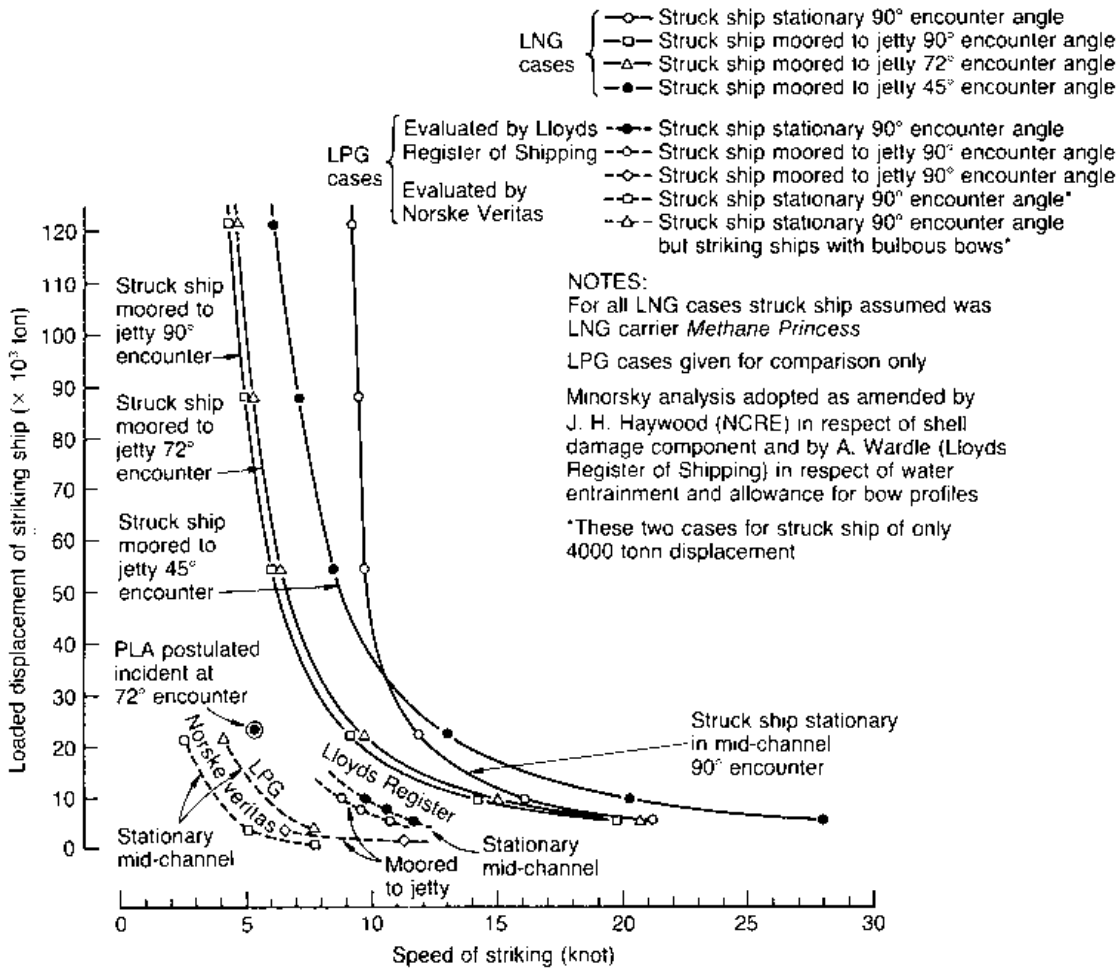


Figure 23.16 *Kinkead model of ship collision: critical impact speeds of ships capable of causing an LNG spill (Kinkead 1978 SRD R91) (Courtesy of the UKAEA Safety and Reliability Directorate)*

Transport Association (IATA). The IATA Restricted Articles Regulations have placed restrictions on the type and quantity of chemicals which are carried and specify requirements for packaging and labelling. These regulations are binding on IATA member airlines and are applied by many which are not members. They are also generally accepted by governments, who apply them to all aircraft registered with them.

In 1983 the International Civil Aviation Organization (ICAO) issued its *Technical Instructions for the Safe Transport of Dangerous Goods by Air* (the *Technical Instructions*). These introduced into air transport the UN system for the classification and packaging of dangerous goods. These *Technical Instructions* have largely superseded the IATA regulations.

In Britain the Air Navigation (Dangerous Goods) Regulations 1985, and subsequent amending regulations, require dangerous goods to be carried in accordance with the *Technical Instructions*. The enforcing authority is the Civil Aviation Authority (CAA).

The IATA continues to publish its Dangerous Goods Regulations. These are broadly compatible with the *Technical Instructions* and continue to be used by many operators.

The *Technical Instructions* give specific instructions for the packaging and set maximum quantities for carriage.

There are some substances the carriage of which is forbidden. These forbidden substances fall into three categories: (1) forbidden unless authorized by the state of origin; (2) forbidden unless authorized by all the states concerned; (3) forbidden in all circumstances. In the UK requests for exemptions must come from the air operator and any exemption is issued to him.

The quantities of hazardous materials moved by air are quite large. In general, the quantities permitted for carriage are larger for cargo than for passenger aircraft.

There has been, however, a steady decline in the proportion of cargo aircraft, so that increasingly carriage is in passenger aircraft.

The carriage of radioactive substances is governed by the IATA Regulations on Radioactive Materials, which embody the International Atomic Energy Agency (IAEA) Regulations on the Safe Transport of Radioactive Materials.

In general, the carriage of hazardous materials does not appear to be a significant cause of, or aggravating feature in, aircraft accidents. However, improperly packed and loaded nitric acid was declared the probable cause of a cargo jet crash at Boston, MA, in 1973, in which three crewmen died (Chementator, 1975 Mar. 17, 20).

Information on aircraft accidents in the USA is given in the NTSB *Annual Report* 1984. In 1984 for scheduled airline flights the total and fatal accident rates were 0.164 and 0.014 accidents per 10^5 hours flown, respectively. For general aviation, i.e. all other civil flying, the corresponding figures were very much higher at 9.82 and 1.73.

23.19.1 Rotorcraft

There is increasing use made of rotorcraft—helicopters and gyroplanes. Although these are used to transport people rather than hazardous materials, it is convenient to consider them here.

An account of accidents is given in *Review of Rotorcraft Accidents 1977–1979* by the NTSB (1981). In 64% of cases (573 out of 889) pilot error was cited as a cause or related factor. Weather was a factor in 17% of accidents. The main cause of the difference in accident rates between fixed wing aircraft and rotorcraft was the higher rate of mechanical failure in rotorcraft accidents.

The NTSB *Annual Report* 1981 gives for rotorcraft an accident rate of 11.3 and a fatal accident rate of 1.5 per 100 000 hours flown.

23.20 Transport Emergency Planning and Spill Control

23.20.1 Emergency planning

The transport of hazardous materials requires emergency planning, but the nature of the emergency plans depends on the mode of transport. Road transport is covered by the CHEMSAFE scheme. Accounts of emergency planning for transport include those in HS(R) 27 and in the ACDS Transport Report (Cooney, 1991) and those by Bosman (1980), Cumberland (1982) and Cooney (1985). The topic is discussed in Chapter 24 and treatment here is limited to two aspects not dealt with there: marine emergencies and spill control.

23.20.2 Marine emergencies

The CIMAH Regulations 1984 contain a requirement for emergency planning for the fixed site to which they are applicable, which may include a port area. The DSHA Regulations 1987, Regulations 26 and 27, require ports handling hazardous substances to undertake emergency planning. HS(R) 27 gives in Appendix 3 detailed guidance for emergency planning in ports.

IMO guidance is contained in *Emergency Procedures for Ships Carrying Dangerous Goods* (IMO, 1991 IMO-254) (EmS). Other guidance is given in *Liquefied Gas Handling Principles on Ships and in Terminals* (SIGTTO, 1986/3), *Guide to Contingency Planning for the Gas Carrier Alongside and within Port Limits* (ICS, 1987/6), *Contingency Planning and Crew Response Guide for Gas Carrier Damage at Sea and in Port Approaches* (ICS, 1989/8), *Guide to Contingency Planning for Marine Terminals Handling Liquefied Gases in Bulk* (ICS, 1989/9) and *Guidelines for the Preparation of Shipboard Oil Spill Contingency Plans* (OCIMF, 1990/9).

Emergency shut-down of ship–shore transfer is covered in *Guidelines for the Alleviation of Excessive Surge Pressure in ESD* (SIGTTO, 1987/4) and *Recommendations and Guidelines for Linked Ship/Shore Emergency Shutdown of Liquefied Gas Cargo Transfer* (SIGTTO, 1987/5).

Fire fighting is covered in *Cargo Firefighting on Liquefied Gas Carriers* (SIGTTO, 1986/2) and *Guide on Marine Terminal Fire Protection and Emergency Evacuation* (OCIMF, 1987/6).

Marine spill control is covered in *Guidelines for the Preparation of Shipboard Oil Spill Contingency Plans* (OCIMF, 1990/9).

23.20.3 Spill control

There are a number of basic techniques for spill control, but there are also some measures which are specific to the mode of transport.

Accounts of spill control are given in *Highly Hazardous Materials Spills and Emergency Planning* (Zadic and Himmelman, 1978) and *Hazards Materials Spills Handbook* (G.F. Bennett, Feates and Wilder, 1982) and by R.L. Mitchell (1971, 1982), R.H. Hiltz (1982), Scholz (1982), H.M. Freeman (1984) and Deckert (1986)

The ease of detection of a spill varies with the mode of transport. The driver of a road tanker will generally know at once. A spill on a rail tank wagon may not be appreciated immediately. A leak from a pipeline may remain undetected for a considerable time.

The general principles of spill control in the field are described by Scholz (1982). The spill may be a continuing escape or a complete spillage of the whole contents. In the former case, the first step is the termination, or at least reduction, of the discharge.

The measures which can be taken to effect this depend on the circumstances. If the leak is below the liquid level, it may reduced by changing the orientation of the tank so that it is vapour rather than liquid which comes out; often, however, this is not practical.

If the source of the leak is a valve, measures may be taken to shut it off. If the leak is from a puncture of the tank itself, it may be possible to plug it. The liquid in the leaking tank may be transferred to another vehicle, either as the prime method of terminating the discharge or after that has been done by some other method. Resort has also been had to dumping the liquid in a pit and then 'neutralizing' it.

It may be possible to plug the leak by bolting on a patch plate. There are also special plugging devices such as the foam plugger developed by the EPA.

Following any measures to effect (1) termination of discharge, the other measures for spill control are (2) containment, (3) suppression of evaporation, (4) removal and (5) disposal.

Whether the spill is a virtually instantaneous release of the whole tank contents or a more gradual leak, the liquid will form a pool on the ground. Priorities are to

prevent the liquid entering drains and sewers, and water courses, and to limit the size of the pool formed.

Depending both on the nature of the material spilled and the population exposed, there may be a need to reduce the rate of evaporation of the liquid pool. General methods of doing this are described below, but they may or may not be practical in a given case.

Methods of removal include pumping and use of sorbents. The pumps used must be able to handle the liquid with which they are presented, which will include not that originally spilled but any added to control evaporation with, possibly, earth and other solid matter. Sorbents include straw and synthetic sorbents. The material recovered is transferred to temporary storage and then passes to disposal.

Spill control measures which are available in principle may be impractical in many transport situations, because they require additional equipment or materials, or for some other reason. Accounts are available of measures actually used in the field, including those of R.L. Mitchell (1982) and Scholz (1982).

23.20.4 Spill control: evaporation

As just described, it may be necessary for highly hazardous materials to take measures to reduce the rate of evaporation. An account of methods available to do this is given by R.H. Hiltz (1982). They include the use of (1) liquid phase modification, (2) surface cooling, (3) mechanical covers, (4) films and foams and (5) sorbents.

For some liquids, the rate of evaporation may be reduced by modifying the liquid phase in some way. Some basic principles are dilution with water, reaction with another chemical and turning the liquid into a gel by use of a gelling agent.

Dilution with water can be effective in some cases, provided the spilled liquid is miscible with water and the pool is sufficiently well confined that addition of water does not cause it to spread.

There is available a Universal Gelling Agent which for a number of substances has been shown to be effective in forming a gel. These substances include water, gasoline and sulphuric acid. An account of this work is given by Pilie *et al.* (1975) and Baier *et al.* (1975/76) and the list of substances is quoted by R.H. Hiltz (1982). Hiltz states that although the formation of a gel may reduce the rate of evaporation, its value lies primarily in effecting immobilization of the spill. Further, the usefulness of the technique may be limited by the time taken for the gel to form. Few gels form within minutes and some take hours.

The vapour pressure of the liquid, and hence the evaporation, may be reduced by cooling the liquid surface, using ice, dry ice or liquid carbon dioxide. To be effective, this method requires good mixing of the coolant and the liquid.

One form of mechanical covers is cloth covers. Another is particulate covers such as small plastic spheres or the like. Sprays based on materials such as urethane are also sometimes classed as mechanical covers.

Films provide essentially a two-dimensional cover and foams a three-dimensional one. Surfactant films act partly by film resistance and partly by quiescence. They may be applied as a spray or in the form of a foam which rapidly collapses. There is a wide variety of foams and a good deal of work has been done to assess their suitability for the control of the evaporation of particular chemicals. Accounts include those of Baier *et al.* (1975), R.H. Hiltz and Friel (1976), Gross (1978), Norman and Dowell (1978), R.H. Hiltz (1982, 1987) and R.H. Hiltz and Brugger (1989). A matrix of foam suitability is given by R.H. Hiltz (1982). This shows high expansion surfactant foam as the best formulation for many of the substances listed, including gasoline, LNG, chlorine and ammonia.

Sorbents are used both to reduce evaporation and to remove spilled liquid. With regard to the former function, the sorbent needs to be continuously replenished. If it is simply allowed to become saturated, it may be ineffective in reducing, and, by increasing the surface area, may even promote vaporization.

23.20.5 Spill control: road transport

The control of a spill from a road tanker illustrates many of the basic principles of spill control. An account of the control of chlorine spills has been given by R.L. Mitchell (1982), with particular reference to the work in the USA of the Chlorine Institute.

The methods which he describes include: shutting off leaking valves; plugging or patching of punctures; transferring the load; and dumping the load into a pit and then neutralizing it.

A large proportion of cases involve leaking valves. The handling of a spill situation is greatly facilitated if the valves and manways are standardized. As Mitchell describes, for the carriage of chlorine in the USA standardization of these items has been achieved for both rail tank cars and tank trucks. The Chlorine Institute has developed a number of emergency kits which include the equipment to assist in valve shut-off.

Some measures may be taken immediately by the tanker driver such as notifying the incident, clearing the area and, if possible, creating temporary diking to divert or contain the liquid spill. Others such as load transfer or dumping and neutralization require additional equipment and/or materials and need to be undertaken by a trained team.

23.20.6 Spill control: pipelines

For pipelines spill control is treated in *Methods of Prevention, Detection and Control of Spillages in West European Oil Pipelines* (CONCAWE, (1987 1/87) and spill clean-up in *Revised Inland Oil Spill Clean-up Manual* (CONCAWE, 1981 7/81).

CONCAWE 1/87 deals with causes of spillage, which are, essentially: mechanical failure, operational failure, corrosion, natural hazards and third party activity (TPA); prevention by design, construction and operation; detection by visual observation monitoring of pipeline parameters; control by operational measures; and emergency procedures.

Pipeline parameters which may provide an indication of a leak, and which may be monitored for this purpose, include pressure and flow. A leak may be detected by a fall in pressure or flow, or an excursion of the volume balance. Other methods of detection are based on negative pressure waves and on ultrasonic noise. Pipeline leak detection is discussed further in Chapter 19.

Table 23.44 *Some principal incidents in the road transport of hazardous materials*

A LNG

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*[a]
1971, Jun. 25	Waterbury, VT	Blowout, leak		Davis
1971, Aug. 28	Warner, NH	Crash (SV), leak		Davis
1971, Oct. 8	N. Whitehall, WI	Crash (TV), petrol and tyre fire		Davis
1973	Junction 80/95, NJ	Crash (SV)		Davis
1973, Oct.	Raynham, MA	Crash (TV), trailer overturn		Davis
1974, Feb. 18	Hamilton Tnpk, NJ	Wheel fire, leak		Davis
1975, Nov.	Dalton, GA	Crash (SV)		Davis
1976, Jan.	Chattanooga, TN	Trailer overturn		Davis
1976, Sep. 16	Pawtucket, RI	Crash (TV), tanker o/turn		Davis
1977, Mar./Apr.	Connecticut Tnpk	Crash (TV)		Davis
1977, Jul.	Waterbury, CT	Crash (TV), trailer o/turn		Davis

B LPG

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*[a]
1943, Jan. 18	Los Angeles, CA	VCF	5d	Table A1.2
1948, Oct. 13	Sacramento, CA	Fire	2d	Table A1.2
1950, Aug.	Wray, CO	VCF	2d	Table A1.2
1958, Oct. 18	Littlebury	Fire		Davis
1962, Jul. 25	Berlin, NY	VCE	10d, 17i	Table A1.2
1970, Nov. 12	Hudson, OH	Fire	6d	Table A1.2
1972, Mar. 9	Lynchburg, VA	Fireball	2d, 5i	Table A1.2
1972, Sep. 21	NJ Turnpike, NJ	Fire	2d, 28i	Table A1.2
1973, Feb. 1	St Amand, France	VCE	9d, 37i	Table A1.2
1974, Feb. 2	High Prairie, Alberta	Fire, explosion	1d, several i	Davis
1975, Apr. 30	Eagle Pass, TX	Fireball	17d, 34i	Table A1.2
1978, Jul. 16	Tula, Mexico	Explosion		Table A1.2
1978, Jul. 15	Xilatopic, Mexico	VCF	100i, 220i	Table A1.2
1982, Dec. 29	Florence, Italy	Explosion	5d, 30i	Table A1.2
1990, Sep. 24	Bangkok, Thailand	VCF	68d, >100i	Table A1.2

C Other

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*[a]
1956, Aug. 7	Cali, Columbia	Explosives explosion	≈1200d	Table A1.2
1968, Aug. 21	Lievin, France	Ammonia leak	5d, 20i	Table A1.2
1970, May 30	Brooklyn, NY	Oxygen leak, fire	2d, 30i	Table A1.2
1975, Dec. 14	Niagara Falls, NY	Chlorine leak	4d, 80i	Table A1.2
1976, May 11	Houston, TX	Ammonia leak	6d, 178i	Table A1.2
1976, Sep. 11	Westoning, UK	Petrol explosion	3i	Table A1.2
1978	Mexico City	Propylene fire	12d	Table A1.2
1978, Jul. 11	San Carlos, Spain	Propylene fire	216d, 200i	Table A1.2
1980, Nov. 25	Kenner, LA	Gasoline fire	7d, 6i	Table A1.2
1980, Mar. 3	Los Angeles, CA	Gasoline BLEVE	2d, 2i	Table A1.2
1982, May 3	Galdecott Tunnel, CA	Gasoline fire	7d	Table A1.2
1989, Mar. 22	Peterborough, UK	Explosives explosion	1d, 107i	Table A1.2

BLEVE, boiling liquid expanding vapour explosion; SV, single vehicle; TV, two vehicle; VCE, vapour cloud explosion; VCF, vapour cloud fire.

[a] L.N. Davis (1979).

Table 23.45 *Some principal incidents in the rail transport of hazardous materials*

A LPG

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*
1949, Oct.	Winthrop, MO	Fire	1d	Table A1.2
1959, Jun, 2	Deer Lake, PA	BLEVE	11d, 10i	Table A1.2
1959, Jun. 28	Meldrin, GA	VCE	23d	Table A1.2
1969, Jan. 25	Laurel, MS	BLEVE	2d, 33+i	Table A1.2
1970, Jun. 21	Crescent City, IL	BLEVE	66i	Table A1.2
1973, Jul. 5	Kingman, AZ	BLEVE	13d,95i	Table A1.2
1973, Nov. 6	Ventura County, CA	Leak	2d, 4i	Table A1.2
1974, Feb. 12	Oneonta, NY	BLEVE	25i	Table A1.2
1975, Oct. 22	Fertile, MN	BLEVE		Davis
1976, Nov. 26	Belt, MT	BLEVE	22i	Table A1.2
1977, Jun. 2	Kent, OH	Explosion		Davis
1978, Feb. 24	Waverly, TN	BLEVE	16d, 43i	Table A1.2

B Chlorine

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*
1914	Chrome, NJ	Leak	0d	Table A1.2
1934, Feb. 28	Niagara Falls, NY	Leak	0d	Table A1.2
1935, Mar. 13	Griffith, IN	Leak	0d	Table A1.2
1940, Jan. 26	Mjodalen, Norway	Leak	3d	Table A1.2
1947, Feb. 4	Chicago, IL	Leak	0d	Table A1.2
1961, Jan. 31	La Barre, LA	Leak	1d, 114i	Table A1.2
1962, Nov. 30	Cornwall, Ont.	Leak	89i	Table A1.2
1963, Apr. 28	Brandtsville, PA	Leak	0d	Table A1.2
1963, Aug. 9	Philadelphia, PA	Leak	430+i	Table A1.2
1967, Nov. 8	Newton, AL	Leak	0d	Table A1.2
1973, Mar. 5	Loos, BC	Leak	0d	Table A1.2
1978, Feb. 26	Youngstown, FL	Leak	8d, 114i	Table A1.2
1979, Nov. 19	Mississauga, Ont.	Leak	Mass evacuation	Table A1.2
1981, Aug. 1	Montana, Mexico	Leak	17d, 280i	Table A1.2

C Other materials

Date	*Location*	*Incident*	*Deaths/injuries*	*Reference*
1915, Sep. 27	Ardmore, OK	Petrol fire	40d	Table A1.2
1943, Jul. 29	Ludwigshafen, Germany	Butadiene VCE	57d, 439i	Table A1.2
1948, Jul. 23	Ludwigshafen, Germany	DME VCE	207d, 3818i	Table A1.2
1958, Jan. 22	Niagara Falls, NY	Nitromethane explosion	200i	Table A1.2
1969, Feb. 18	Crete, NE	Ammonia leak	9d, 53i	Table A1.2
1969, Sep. 11	Glendora, MS	VCM leak, VCE	1i	Table A1.2
1974, Jun. 26	Climax, TX	VCM VCE	7d	Table A1.2
1974, Jul. 19	Decatur, IL	Isobutane VCE	7d, 152i	Table A1.2
1974, Sep. 21	Houston, TX	Butadiene VCE	1d, 235i	Table A1.2
1974, Aug. 6	Wennatchee, WA	MMN explosion	2d, 113i	Table A1.2
1978, Sep. 27	Oviedo Province, Spain	Gasoline fire	7d	Table A1.2
1979, Apr. 8	Crestview, FL	HMs leak	14i	Table A1.2
1983, Nov. 2	Dhurabar, India	Kerosene explosion	47d	Table A1.2
1987, Aug. 23	Lhanzou, China	Gasoline fire	5d	Table A1.2

BLEVE, boiling liquid expanding vapour explosion; DME, dimethyl ether; HM, hazardous materials; MMN, monomethylamine nitrate; VCE, vapour cloud explosion; VCM, vinyl chloride monomer.
[a] L.N. Davis (1979).

Emergency procedures for dealing with a pipeline spill include: notification of the leak; actions to reduce or stop the flow; location of the leak point; and measures to stop the hole.

Spill clean-up is treated in CONCAWE 7/81 under the headings of (1) behaviour of oil spills, (2) identification of contaminated zones, (3) clean-up strategy, (4) clean-up methods for oil on ground surfaces, (5) clean-up methods for subsoil, (6) clean-up methods for ground waters, (7) clean-up methods for surface waters, (8) clean-up methods in ice and snow, (9) integrated clean-up methods and (10) emergency kits for inland oil spills.

23.21 Transport Case Histories

23.21.1 Packaging and labelling

Misidentification of chemicals can have very serious consequences. This was highlighted by the *Firemaster* tragedy in Michigan in 1973, which has been described in *Bitter Harvest, The Poisoning of Michigan* (Egginton, 1980) and by Getty, Rickert and Trapp (1977), Kay (1977) and Selikoff (1979). A consignment of *Firemaster*, a fire-retardant chemical (polybrominated biphenyl (PBB)), was dispatched from the Michigan Chemical Company instead of an animal feed additive which had a rather similar name. The consequences were a serious contamination of food eaten by animals and humans throughout much of the state. Cattle showed severe symptoms of poisoning. Somewhat similar symptoms were also found among residents of the state.

23.21.2 Road transport

Some principal incidents in the road transport of hazardous materials are shown in Table 23.44. Many of these incidents are described in Chapters 16–18 on fire, explosion and toxic release or are given in the case histories in Appendix 1.

In particular, attention is drawn to: the incidents at Deer Lake in 1959 (Case History A27) and Eagle Pass, Texas, in 1975 (Case History A76) involving BLEVEs and/or fireballs; those at Berlin, New York, in 1962 (Case History A30), at Lynchburg, Virginia, in 1972 (Case History A59) and at St Amand-les-Eaux, France, in 1973 (Case History A66), involving vapour cloud explosions; and those at Lievin, France, in 1968 and Houston, Texas, in 1976 (Case History A84), involving toxic releases.

On 14 July 1978 a road tanker carrying propylene ruptured near a camp site at San Carlos de la Rapita, Spain, and there was a flash fire which resulted in an eventual death toll of some 210 people (Appendix 16).

23.21.3 Rail transport

Some principal incidents in the rail transport of hazardous materials are shown in Table 23.45. Many of these incidents are described in Chapters 16–18 on fire, explosion and toxic release or are given in the case histories in Appendix 1.

In particular, attention is drawn to: the incidents at Crescent City, Illinois, in 1970 (Case History A50), Kingman, Arizona, in 1973 (Case History A63), Belt, Montana in 1976 and Waverly, Tennessee in 1978 (Case History A93), involving BLEVEs and/or fireballs; those at East St Louis, Illinois in 1972 (Case History A57) and at Decatur, Illinois, in 1974 (Case History A71), involving vapour cloud explosions; those at La Barre, Louisiana in 1961 (Case History A29) and at Cornwall, Ontario, in 1962, at Crete, Nebraska in 1969 and at Youngstown, Florida in 1978 (Case History A94), involving toxic releases; and that at Glendora, Mississippi in 1969 (Case History A43), involving a major evacuation.

On 10 November 1979 a freight train fire occurred in a built-up area of Mississauga, Toronto (Case History A97). The fire was on a tank car containing flammable liquid, but the hazard was much increased by the fact that an adjacent tank car contained chlorine. A major evacuation took place. In fact the emergency response was effective and the incident was contained, but the incident showed the importance of segregating flammable and toxic substances, so that a fire involving the former does not put the latter at risk.

A derailment of a freight train occurred on 28 September 1982 at Livingston, Louisiana (Case History A103). Some 43 cars were derailed and there was a massive fire. A cause of the accident was the misapplication of the brakes by an unauthorized rider in the locomotive cab, a clerk who was 'substituting' for the driver. The driver was found to have consumed a large amount of alcohol shortly beforehand.

There have also been incidents in tunnels. On 20 December 1984 a train conveying 835 te of petrol derailed in the Summit Tunnel, near Todmorden, Yorkshire (A. Jones, 1985). A spill occurred and was ignited, giving rise to a fire. One tank wagon suffered a BLEVE. The fire, which reached a mean temperature of 1300°C and 1530°C in places, destroyed the train and severely damaged the 2638 m long tunnel. Columns of flame and smoke rose high above the ventilation shafts.

23.21.4 Waterway transport

Some principal incidents in the inland waterway transport of hazardous materials are shown in Table 23.46.

A collision on the Seine, below Rouen, between the two product tankers *Foyoh Maru* and *Vitoria*, in ballast after discharging a cargo of gasoline, resulted in a violent explosion on the latter killing six of the crew. The vessel itself broke in two and was completely destroyed, whilst fragments from it fell over a wide area.

On 30 August 1979 near Good Hope, Mississippi, the MV *Inca Tupac Yupanqui* lost steering and collided with the butane tank barge *Panama City* moored at a dock (Case History A96). The freighter's bow struck the barge amidships, cutting it in two and causing a fire and explosion which killed 12 people and did extensive damage to the dock. Half the butane barge drifted downstream and continued burning for about 24 hours.

Table 23.46 *Some principal incidents in the inland waterway transport of hazardous materials*[a]

Date	*Location*	*Incident*	*Deaths/injuries*
1978, Oct. 3	Pilottown, LA	*Burmah Spar* – collision with vessel	
1979, Aug. 30	Good Hope, MS	*Panama City* – collision with vessel	12d, 25i
1980, Mar. 29	New Orleans, MS	*Exxon Baltimore* – collision with vessel	
1980, Dec. 12	New Orleans, MS	*Pisces* – collision with vessel	
1983, Apr. 2	St Louis	*City of Greenville* – collision with bridge	

[a] Source: NTSB *Annual Reports* 1979–84.

At St Louis on 2 April 1983 a four–barge tow pushed by the towboat *City of Greenville* hit a bridge, causing the breakway of three barges and an oil spill fire. The burning barges caused further fires along a 2–mile stretch of the river front. A year later on 24 April 1984 the same bridge was hit by a 12–barge tow of grain barges and a breakway of these barges resulted in a chain reaction of other barge breakaways along the waterfront until some 150 barges were adrift.

23.21.5 Pipeline transport

There have been a number of major accidents arising from the pipeline transport of hazardous materials.

One of the worst disasters in the process industries was a pipeline accident. On 24 February 1984 petrol leaked from a pipeline passing through a shanty town at Cubatao, Brazil, forming a large liquid pool which then ignited (Case History A108). The death toll is uncertain, but is believed to have run to some hundreds.

An explosion on a natural gas pipeline at Natchitoches, Louisiana, on 4 March 1965 caused a massive split in the pipe and killed 17 people (Case History A37).

A leak of propane from a ruptured 8 in. pipeline at Port Hudson, Missouri, on 9 December 1970 resulted in a massive vapour cloud explosion (Case History A52).

At Hearne, Texas, on 14 May 1972 a rupture on an 8 in. oil pipeline led to a flowing liquid fire (Case History A58).

A rupture of a 10 in. NGL pipeline at Austin, Texas, on 22 February 1973 resulted in the formation of a vapour cloud which ignited some 20 minutes later, killing six people (Case History A62).

On 13 March 1990 a gas cloud formed from a rupture of a liquid propane pipeline flowed downhill into the village of North Blenheim, New York (NTSB, 1991 PAR-91–01) . The cloud ignited, flashing back to the pipeline rupture. Two people were killed.

Another major pipeline disaster occurred on 3 June 1989 at Ufa in Western Siberia (Case History A127). A leak occurred from a pipeline carrying mixed LPG near a railway line. A massive vapour cloud formed and ignited as two trains were passing. The strength of the explosion has been estimated as equivalent in the far field to 10 000 te of TNT. Initial reports put the death toll at 462, with many others severely burned.

An incident involving a vapour leak on an ammonia pipeline occurred on 6 December 1973 near McPherson, Kansas (Case History A64).

23.21.6 Marine transport

The case histories considered here may be classed as: collisions, groundings and driftings; lightning strikes, fires and explosions; and oil spillages.

On 9 November 1974 the oil/LPG carrier *Yoyo Maru* was in collision in Tokyo Bay with the cargo ship *Pacific Ares*. A 24 m gash was cut in the *Yoyo Maru*'s hull and naphtha spilled out and ignited, giving a fire with flames 70 m high. The vessel also had LPG in other cargo tanks, but the LPG tanks and fittings withstood the fire, although LPG from the tank vents burned. Fire-fighting vessels were for some time unable to approach close due to the heat. The vessel was towed out to sea, where it continued to burn and was eventually sunk by air strikes. The death toll was 33.

In some cases collisions occur while the vessels are proceeding at full speed. On 9 February 1982 off North Carolina the barge carrier *Lash Atlantico* and the freighter *Hellenic Carrier* were in collision in thick fog as both vessels were at full speed. There were no injuries, but both vessels were badly damaged, the latter beyond repair. Ten days later the barge carrier *Del Norte* and the freighter *African Pioneer* collided in the Gulf of Mexico, again both moving at full speed in thick fog. This time there were two serious injuries and again both ships were severely damaged.

On 21 August 1980 the tanker *Texaco North Dakota* travelling at full speed struck a partially constructed oil platform in the Gulf of Mexico (NTSB, 1981 MAR-81–04). The tanker was partly loaded with petroleum products, several cargo tanks were ruptured and fire broke out which gutted the vessel.

On 6 March 1982 the tankship *Golden Dolphin* exploded, burned and sank in the Atlantic 1000 miles to the south-east of Bermuda (NTSB, 1983 MAR-83–07). The vessel was in ballast and an empty cargo tank was being cleaned when a series of massive explosions occurred. An inert gas system had just been fitted but was not in use. The crew abandoned ship but nine died.

On 27 February 1984 in the Gulf of Mexico the tanker *American Eagle* was wracked by an explosion and broke up (NTSB, 1985 MAR-85–06). Three crew died in the explosion, and two more died later and two were missing in the sinking.

Some shipboard fires and explosions are caused by lightning strikes. On 19 April 1979 the tankship *Seatiger* was hit by lightning while unloading oil at Port Neches, Texas (NTSB, 1980 MAR-80–12). Most of the cargo tanks exploded and the ship was destroyed. A similar explosion occurred on 1 September 1979 at Deer Park, Texas, when the tankship *Chevron Hawaii* exploded while unloading oil at a refinery (NTSB, 1980 MAR-80–18). Lightning ignited flammable cargo vapours on deck which propagated into an empty cargo tank, where the explosion occurred. Amongst the many fragments was a 15×2.1 m section of hull which penetrated an onshore ethanol tank 250 m away. Burning cargo spread across the water and ignited the contents of three petroleum barges, which exploded and sank. Casualties are variously given as 3 or 4 killed and 9 to 13 injured.

Incidents of fires and explosions on chemical tankers with special reference to ignition in cargo tanks due to static electricity have been given by M.R.O. Jones and Bond (1984).

Some of the worst disasters due to chemicals have been shipboard explosions of ammonium nitrate. On 16 April 1947 a fire broke out on an ammonium nitrate vessel, the *Grandcamp*, in Texas City Harbor (Case History A16). After about an hour the ship disintegrated with a tremendous explosion, killing all those in the dock. Fire spread to another vessel, the *High Flyer*, which also carried ammonium nitrate, and during the night this vessel too exploded. There were 552 deaths and over 3000 injuries.

On 8 January 1979 a large explosion and fireball occurred on board the *Betelgeuse* which was unloading at an oil terminal at Whiddy Island, Bantry Bay, Eire (Case History A95). All 42 members of the crew were killed as well as a crewman's wife and seven terminal operators.

Table 23.47 *Some principal incidents to LFG carriers*

A Groundings, strandings, driftings

Date	*Location*	*Vessel*	*Cargo*	*References*[a]
1966, May 1	Thames	*Methane Progress*	LNG	Cox
1968, Sep.	Mexico	*Aristotle*	LNG	Davis
1974, Apr. 19	Arzew, Algeria	*Methane Progress*	LNG	Cox
1974, Oct. 28	Rhone Delta, France	*Hassi R'Mel*	LNG	Cox
1974, Nov.	Le Havre, France	*Euclides*	LNG	Davis
1978, Jan. 11	Canvey, UK	*LNG Aries*	LNG	Davis
1979, Sep. 30	Takari Bay, Lagos, Nigeria	*Babounis Costas*	LPG	Lakey
1980, Dec. 12	Mutsure Anchorage, Tobata, Japan	*LNG Taurus*	LNG	Lakey
1981, Dec. 16	Cape Sable Island Nova Scotia	*El Paso Columbia*	LNG	Lakey

B Collisions, rammings, impacts

Date	*Location*	*Vessel*	*Cargo*	*References*[a]
		Methane Princess	LNG	Cox
1968, Autumn	Southampton, UK	*Claude*	LPG	Davis
1968, Sep. 12	Flushing, Belgium	*Havfrost*	LPG	Harris[b]
1968, Dec. or 1969, Jan.)	Canvey, UK	*Methane Princess*	LNG	Davis
1969, Feb. 10		*Methane Princess*	LNG	Cox
1969, Feb. 25	Straits of Malacca	*Gohshu Maru*	LPG	Harris
1970, Oct. 19		*Methane Progess*	LNG	Cox
1970, Oct. 21	Konigsforde, W. Germany	*Mariotte*	LPG	Harris
1971, Jun. 17	Tokyo Bay, Japan	*Gohshu Maru*	LPG	Harris
1972, Jul. 21	Heroya, Norway	*Monomer Venture*	LPG	Harris
1973, Jan. 14	Bilbao, Spain	*Alexander Hamilton*	LPG	Harris
1973, Mar. 28	Straits of Malacca	*World Bridgestone*	LPG	Harris
1973, Dec. 16	Ras Tanura, Saudi Arabia	*Beava*	LPG	Harris, Lakey
1974, Aug.	Terneuzen, Belgium	*Euclides*	LNG	Davis
1974, Nov. 9	Tokyo, Japan	*Yoyo Maru*	LPG	Davis, Harris, Lakey
1974, Dec. 6	London, UK	*Methane Progess*	LNG	Cox
1975, Jun. 9	Buenos Aires, Brazil	*Gazana*	LPG	Harris
1975, Jul. 14	Pentland Firth, UK	*M.P. Grace*	LPG	Harris
1977, Jun. 7	Bahrain	*LNG Challenger* and *Lincolnshire*	LNG	Davis
1978, Aug. 14	Singapore	*Khannur*	LNG	Davis
1978, Aug. 26	Bahrain	*LNG Challenger*	LNG	Davis
1978, Oct. 29	Suez Canal	*Lord Kelvin*	LPG	Harris
1980, Jan. 30	Singapore	*Pine Queen*	LPG	Harris
1980, Feb. 19	Porto Marghera, Italy	*Gazana*	LPG	Harris
1982, Jan. 24	Curacao	*Faraday*	LPG	Harris
1982, Apr. 28	Cristobal, Panama	*Luigi Casala*	LPG	Harris
1983, Apr. 3	Tampico, Mexico	*Reynosa*	LPG	Harris
1983, Aug. 3	Yugecho, Japan	*Kazutama Maru*	LPG	Harris
1985, Apr. 11	Choshi, Japan	*Berge Arrow*	LPG	Harris
1985, May 31	Coatzacoalcos	*Mariano Escobedo*	LPG	Harris

C Leaks

Date	*Location*	*Vessel*	*Cargo*	*References*[a]
1965		*Methane Princess*	LNG	Lakey
1965, May		*Jules Verne*	LNG	Lakey
1969, Nov. 19		*Polar Alaska*	LNG	Cox
1974, Dec.		*Jules Verne*	LNG	Cox

1975, May 1		*Methane Progess*	LNG	Cox
1976, Dec. 20	Kenai	*Polar Alaska*	LNG	Cox
1977, May 14	Chiba, Japan	*Hilli*	LNG	Cox
1977, Sep. 16	Bontang	*LNG Aquarius*	LNG	Lakey
1979, Apr. 8	Cove Pt, MD	*Mostafa Ben Boulaid*	LNG	Lakey
1979, Apr. 25	Everett, MA.	*Pollenger*	LNG	Lakey
1981, Jul. 31	Sines, Portugal	*Olav Trygvason*	LNG	Lakey
Voyage 2		*Descartes*	LNG	Cox

D Lightning strike and fire

Date	*Location*	*Vessel*	*Cargo*	*References*[a]
1964, Dec. 25		*Methane Progress*	LNG	Lakey
1965	Nr Arzew, Algeria	*Methane Progress*	LNG	Lakey
1977, Sep. 3	Tobata, Japan	*LNG Aquarius*	LNG	Lakey
Unknown		*Jules Verne*	LNG	Lakey

E Other incidents

Date	*Location*	*Vessel*	*Cargo*	*References*[a]
1964 Small fire		*Methane Princess*	LNG	Cox
1966, Aug. 30 Small fire		*Methane Princess*	LNG	Cox
1971, Sep. 14 Weather damage to tank		*Arctic Tokyo*	LNG	Cox
1974, Jun. Pump room explosion	Grangemouth, UK	*Milli*	LPG	Davis, Lakey
1974, Jul. 7 Valve overpressurized, canopy cracked		*Massachusetts*	LNG	Cox
1976, Dec. 1 Broke moorings	Marseilles, France	*Benjamin Franklin*	LNG	Cox
1978, Oct. 10 Pump fire	Donges, France	*Danian Gas*	LPG	Lakey
Voyage 2 Overfilling, deck brittle fracture		*Jules Verne*	LNG	Cox

[a] R.A. Cox, Comer *et al.* (1980); L.N. Davis (1979); F.S. Harris (1986); Lakey and Thomas (1983).
[b] LPG vessels in incidents quoted by Harris were all refrigerated carriers.

Further case histories of fire and explosion on vessels in port are given by Rushbrook (1979) and by Dicker and Ramsey (1983).

Large scale oil spills are a major threat to the environment. Major oil spills are those from the *Torrey Canyon* in 1967, the *Amoco Cadiz* in 1978, the *Exxon Valdez* in 1989 and the *Braer* in 1993. Further details are given in Appendix 11.

23.21.7 Marine transport: LFG

Some principal incidents to LFG carriers are given in Table 23.47. An account of incidents involving LNG carriers has been given by Lakey and Thomas (1983). L.N. Davis (1979) describes incidents with both LNG and LPG vessels.

On 29 June 1979 the LNG carrier *El Paso Paul Kayser* ran aground at Gibraltar. The bottom plating on the starboard side was ripped open but, although deformed, the Gaz Transport containment system, including both the primary and secondary containment barriers, remained liquid tight.

Another grounding of an LNG tanker occurred on 12 December 1980 when the *LNG Taurus* ran aground at Mutsure Anchorage, near Tobata, Japan. The initial damage in this case was less, but was aggravated during 4 days aground.

Worse damage than in either of these cases was sustained by the *El Paso Columbia* when it grounded on 16 December 1981 near Cape Sable in Nova Scotia. The engine room and, apparently, one cargo tank were flooded, but the vessel was in ballast.

In the autumn of 1968 the LPG carrier *Claude* collided with another vessel in Southampton Water. The crew abandoned ship and the vessel drifted until it ran aground. Another ship was chartered to remove the cargo of butane, but backed off when one of the unloading hoses sprang a leak, giving a vapour cloud. The leak was stopped by other boarders.

There have been a number of spills of LNG on the decks of LNG carriers. In 1965, fracture of the mild steel deck of the *Methane Princess* occurred due to a small LNG spill. In the same year, at Arzew another LNG carrier, the *Descartes*, also suffered deck fracture from an LNG overfilling.

LNG carriers have also experienced cargo tank rupture. On 17 November 1969 rupture of a cargo tank occurred on the *Polar Alaska* due to violent sloshing of the LNG liquid. In 1970, the LNG carrier *Arctic Tokyo* suffered cracking of a cargo tank due to sloshing.

On 30 June 1974 there was a pump room explosion and fire aboard the semi-refrigerated LPG carrier *Milli* as she began unloading butylene at Grangemouth. A butylene vapour cloud estimated at 50 te spread around the area near the ship. The captain, who was in the pump room, died.

There have been several lightning strikes followed by fires on LNG carriers. On 25 December 1964 this occurred to the *Methane Progess* just after loading at Arzew. The next year the same ship again suffered a lightning strike and fire. In 1977 the *LNG Aquarius* unloading at Tobata, Japan, was struck by lightning followed by fire. Lightning strike and fire have also been experienced by the LNG carrier *Jules Verne*.

On 12 October 1984 the LPG tanker *Gas Fountain*, originally the *Gay Lussac*, was attacked by an Iranian aircraft in the Gulf. Three rockets hit the vessel. The crew abandoned ship and were rescued. One rocket caused a rupture of the pipework of No. 2 tank; propane escaped and caught fire. A second rocket penetrated the deck into the containment space of No. 3 tank and exploded near the cargo tank, creating a hole some 3 m × 2 m. Butane escaped and ignited giving a large fire on deck. It is estimated that some 130 te of butane may have escaped during this initial depressurization. The next day a salvage vessel arrived, extinguished the fires using water jets, and took the vessel in tow. Extensive repairs were carried out. About a month later most of the LPG cargo, some 17 200 of the original 18 400 te, was transferred to another vessel. An account of this salvage is given by J.A. Carter (1986).

23.22 Transport Risk

23.22.1 Historical record

The risks from the process industries arise from processes, storage and transport. The historical record shows that transport is a major contributor. Transport figures prominently in the case histories given in Appendix 1 and elsewhere in this book. An attempt to quantify the contribution made by transport to the overall risks from the process industries is given below.

23.22.2 Hazard assessment

Another approach to the estimation of the risk from transport is hazard assessment. A major hazard assessment exercise for transport is the ACDS *Transport Hazards Report*, which is described in Appendix 17. An account is given below of hazard assessments of transport by the principal modes of road, rail, ship and pipeline for the principal hazardous substances of LNG, LPG, chlorine and ammonia.

23.22.3 Fixed installations vs transport

A study of the relative risks from fixed installations and transport by road, rail, pipeline and waterway and sea has been made by Haastrup and Brockhoff (1990). They identified in the literature 1793 accidents in both fixed installations and transport. The breakdown of the accidents was as follows:

	No. of accidents	*No. of accidents with fatalities*
Fixed installations	998 (56%)	454 (67%)
Loading/unloading	104 (6%)	47 (7%)
Transport	691 (39%)	181 (27%)
Total	1793	682

and for the transport modes

	No. of accidents	*No. of accidents with fatalities*
Road	205 (30%)	54 (30%)
Rail	257 (37%)	41 (23%)
Pipeline	133 (19%)	56 (31%)
Inland waterway	38 (5%)	4 (2%)
Marine	58 (8%)	26 (14%)
Total	691	181

The authors quote the analysis of transport accidents in the Major Hazards Incidents Data Service (MHIDAS) database made by Appleton (1988 SRD R474), who found that 17% involved road, 36% rail and 21% pipelines.

The authors selected for study accidents occurring after 1959, which gave a total of 510 accidents with fatalities. They present a set of frequency–number curves, including one showing an overall world-wide curve for fixed installations and a corresponding curve for all transport modes. The transport curve lies somewhat above that for fixed installations, but for accidents with the number of fatalities exceeding four there was found to be no statistically significant difference between the two curves. Another of the graphs gives a set of separate curves for world-wide transport by road, rail and pipeline. The three curves lie very close to each other.

Some major transport accidents include the ammonium nitrate explosions at Halifax, Nova Scotia, in 1917 and at Texas City in 1947, the road tanker fire at San Carlos in 1978, the pipeline rupture and fire at Cubatao in 1984 and the pipeline rupture and explosion at Ufa in 1989.

23.23 Transport Hazard Assessment

The hazards of transport tend to differ from those of fixed installations, whether process or storage, in a number of ways.

Disregarding pipelines for the moment, transport is characterized by the large amount of energy in the vehicles and vessels, both those carrying the hazardous materials and others. The order of increasing energy is road, rail and marine.

Another difference is the transport environment, which is much less subject to control by management. A transport vehicle or vessel is exposed to a variety of external threats to an extent that the situation is qualitatively different from that on fixed plant.

A third difference is in the variety of locations where an accident may occur and in the population exposed to any incident.

These last two points also apply to some degree to pipelines, but these are fixed installations and tend to have more in common with other fixed installations in the process industries.

The differences between transport and fixed installations are reflected in the hazard assessments. In the hazard assessment of transport the characteristic features tend to be the incident scenarios, the associated frequency estimates and the population models. By contrast, the hazard models used to determine consequences are generally those developed for fixed installations, although there are some special cases such models for explosions in ship cargo holds or for events in tunnels.

As already mentioned, the most comprehensive hazard assessment for transport is the ACDS *Transport Hazards Report*, which is described in detail in Appendix 17. This deals with the risks from transport by road, rail and sea, though not by pipeline, for the set of four study substances motor spirit, LPG, chlorine and ammonia and also for explosives.

Some other hazard assessments of transport are now described.

23.24 Road Transport Hazard Assessment

The road transport environment has been described in Section 23.6. The account given there includes estimates made in the ACDS report of the frequency of release for the four study substances. The substance which has been most intensively studied is chlorine. Accounts of studies on the risks of chlorine transport include those of Westbrook (1974), Lautkaski and Fieandt (1980) and Canadine and Purdy (1989).

The work of Westbrook (1974) has been described in detail in Chapter 18. In this early study of chlorine transport in the UK, the author used data for road tankers generally and obtained the following estimate, which he then applied to chlorine tankers also:

$$\text{Frequency of accidents} = 0.63 \times 10^{-6}/\text{tanker-km}$$

The reference distance is for loaded journeys only. Westbrook then assumed that all tanker accidents are potentially spillage accidents. This approach is therefore very conservative.

Lautkaski and Fieandt (1980) in a study of the road and rail transport of hazardous materials in Finland made the following estimate for road tankers generally:

$$\text{Frequency of releases} = 2 \times 10^{-8}/\text{tanker-km}$$

It is unclear whether the reference distance is for loaded and unloaded journeys or for loaded journeys only. They state that some 15% of releases are due to valve failures and 85% to road accidents.

Canadine and Purdy (1989) describe a hazard assessment of the rail and road transport of chlorine. This study, which is evidently part of the background work preceding the ACDS report, does not explicitly quote release frequencies, although it does give some figures for societal risk. It does, however, provide insight into the factors bearing on a hazard assessment for chlorine road transport.

The principal producer of chlorine in the UK is ICI. The company has some 19 road tankers with payloads of 15–21 te. Over a 60–year period there have been three leaks. Two were due to incompletely closed valves and were quickly rectified and the third was minor.

The frequency with which these tankers are involved in accidents is significantly lower than for commercial transport generally. The vehicles are fitted with various arrangements to reduce the accident rate, such as high quality suspension, anti-skid devices, anti-jack-knife systems, fuel cut-off devices, additional fire protection, and regular lights and fog lights. The tankers have their liquid and vapour valves protected in a recessed valve chest at the front of the vehicle. They have excess flow valves, and the two latest vehicles also have remotely operated shut-off valves.

Since 1976 the company has taken additional measures to reduce the consequences of any collision. Additional rear and side protection has been fitted to resist penetration, absorb energy and spread the load in the case of collision. The value of these measures was illustrated in 1985 when the most serious accident recorded to date occurred. A chlorine tanker was hit by a 38 te articulated lorry travelling at an estimated 60 mph down a hill near Baslow in Derbyshire. The vehicle veered diagonally across the road and hit the chlorine tanker on its front offside, stopping it dead and driving it sideways across the road. The side protection on the tanker absorbed most of the collision energy and spread the load as it was designed to do; there was no leak.

As described in Section 23.6, the ACDS report gives estimates for the road transport of chlorine which distinguish between releases due to punctures and those due to equipment failure. The frequency of the latter is expressed as releases per journey, but using the average journey length quoted, the following estimates for releases from chlorine tankers are obtained

$$\text{Frequency of release due to puncture} = 0.008 \times 10^{-8}/\text{tanker-km}$$

$$\text{Frequency of release due to equipment failure} = 0.003 \times 10^{-8}/\text{tanker-km}$$

$$\text{Frequency of release} = 0.011 \times 10^{-8}/\text{tanker-km}$$

The reference distance is for loaded journeys.

23.25 Rail Transport Hazard Assessment

The rail transport environment has been described in Section 23.8. The account given there includes estimates made in the ACDS report of the frequency of release for the four study substances.

As for road transport, the substance which has been most intensively studied is chlorine. Accounts of studies on the risks of chlorine transport include those of Westbrook (1974), Lautkaski and Fieandt (1980), N.C. Harris and Roodbol (1985), Purdy *et al.* (1988) and Canadine and Purdy (1989).

The early study of Westbrook (1974), described in Chapter 18, on chlorine transport in the UK, used data for freight trains generally combined with a train model for the probability of a release given an accident and obtained for chlorine tank wagons the following estimates:

Frequency of accidents = 1.18×10^{-6}/train-km
Probability of release = 0.041

Hence

Frequency of release = 4.8×10^{-8}/train-km

or for an average of 4 tank-wagons per train

Frequency of release = 1.2×10^{-8}/tank-wagon-km

The reference distance is for loaded journeys only.

In their study for Finland, Lautkaski and Fieandt (1980) made the following estimates for rail tankers generally:

Frequency of releases = 0.41×10^{-8}/tank-wagon-km

The reference distance is unclear. This figure excludes releases due to valve failure, which the authors state amounts in the case of rail transport to 99.5% of all releases. They also say that the additional protective features of chlorine tank wagons were considered, but do not state what allowance, if any, was made for them.

N.C. Harris and Roodbol (1985) describe a hazard assessment of the rail transport of chlorine for the Netherlands. The accident and release estimates which they quote include the following values:

Country	*Event frequency*		
	Accident (train-km)	*Minor release* (tank-wagon-km)	*Major release* (tank-wagon-km)
UK	0.35×10^{-6}	1×10^{-8}	
Netherlands	0.88×10^{-6}	1×10^{-8}	0.1×10^{-8}
USA	6×10^{-6}	6×10^{-8}	1.5×10^{-8}

The reference distance is unclear.

Purdy *et al.* (1988) describe the hazard assessment of chlorine rail transport. This study, which is evidently part of the background work preceding the ACDS report, resembles the treatment given in the latter and is not therefore considered further here.

Another precursor to the ACDS report, the work of Canadine and Purdy (1989), deals with rail as well as road transport of chlorine. As for the road study, figures are given for societal risk though not for release frequency, but the account provides insight into the relevant factors.

The principal chlorine producer, ICI, operates some 40 braked tank wagons which take a 28 te load. This contrasts with the fleet of about 300 unbraked tank wagons of 14 te capacity in the 1950s. The company has never experienced puncture of a chlorine rail tank wagon or a major release.

The older type of tank wagon was involved in some major collisions, including one in which a loaded wagon travelling at 60 mph demolished a signal box, though it did not leak. Since the introduction of the larger wagons, accidents have been limited to minor derailments and collisions in marshalling yards.

The modern wagons have a number of safety features. They are fitted with top mounted needle valves, each with an internal excess flow valve, and protected with a heavily reinforced low profile dome. They are provided with buffer override protection consisting of a reinforced hollow steel section mounted below the buffers across the width of the tank.

As described in Section 23.8, the ACDS report gives estimates for rail transport of chlorine which distinguish between releases due to punctures and those due to equipment failure. The frequency of the latter is expressed as release per journey, but using the average journey length quoted, the following estimates for releases from chlorine tank wagons are obtained:

Frequency of release due to puncture = 0.09×10^{-8}/tank-wagon-km
Frequency of release due to equipment failure = 0.02×10^{-8}/tank-wagon-km
Frequency of release = 0.11×10^{-8}/tank-wagon-km

The reference distance is for loaded journeys.

23.26 Tunnel Transport Hazard Assessment

Studies of road tunnel hazards include those of the Larson, Reese and Wilmot (1983) and Considine (1986), and several others referenced by the latter.

In the study by Considine (1986), the two principal events considered are spills and fires. For the estimation of the frequency of these events, the approach adopted was to extrapolate from open route data, the information on incidents in tunnels being inadequate. The author's estimates for road tankers are as follows:

Frequency of spills from tankers = 5×10^{-8}/tanker-km
Frequency of fires on tankers = 1×10^{-8}/tanker-km

He states that for vehicles carrying packages the frequency of spills is about twice, and that of fires about half, the above figures. Many package spills occur when the package falls off the vehicle.

Events in tunnels may be initiated by a leak from a container, an explosion in a container, a fire of the load or an explosion of the load. The scenarios considered are fire, explosions (physical, condensed phase and vapour cloud) and toxic release.

The hazard models used to predict the consequences are for the most part adaptations of those developed for events in the open. For pool spread, a two-dimensional adaptation of the SPILL code was utilized. Gas dispersion is dominated by the tunnel ventilation. For heavy gas

dispersion, use was made of a two-dimensional adaptation of the DENZ and CRUNCH codes for instantaneous and continuous releases, respectively, with the cloud advected at the ventilation velocity. For physical explosion the code GASEX was used. For condensed phase explosions, empirical correlations given in Christopherson (1946) were used to predict overpressure and impulse as a function of charge size, tunnel cross-section and distance. For vapour cloud deflagration, a simple combustion model was used based on a constant flame velocity and shock velocity, followed on completion of combustion by transition to a one-dimensional fluid flow code.

Four tunnels were studied. The data given include the following:

	Tunnel 1	*Tunnel 2*	*Tunnel 3*	*Tunnel 4*
Length (m)	1030	1483	1436	650
No. of tubes/lanes per tube	2/2	1/2	1/2	2/3
Lane width (m)	3.65	2.41	3.65	3.65
Headroom (m)	5.1	4.72	5.03	5.1
Ventilation system	Longitudinal	Semi-transverse	Semi-transverse plus section of longitudinal	Longitudinal
Construction	Submerged section	Driven tube	Driven tube	Cut and cover

An explosion may cause damage to the tunnel. In general, experiments indicate that damage in a large tunnel correlates better with mean overpressure than with transient peak overpressures. For the condensed phase explosions, peak overpressures were high, but the serious structural failures predicted were limited to two tunnels. These failures were of the roof and median wall in Tunnel 4 and of the road support in Tunnel 3 and were confined to a few tens of metres. The effects did not worsen dramatically for increasing charge sizes. The most damaging event was found to be deflagration of a vapour cloud filling the whole cross-section along an appreciable length. The effects obtained were comparable with those of a TNT explosion, but with a longer section sustaining damage. For injury from explosions, use was made of the injury relations given by Eisenberg, Lynch and Breeding (1975) and by W.E. Baker *et al.* (1979).

A fire in a tunnel differs in its effects from one in the open in that the flames, hot gas and smoke are confined and are thus much more lethal. Persons exposed are principally other road users and the general public.

The results of the hazard assessment included the following findings. The risks are mainly to other road users, those to the general public being typically an order of magnitude less. The dominant contributor ($>70\%$) to these risks is flammable liquids.

At the lower end of the spectrum ($N \geq 1$ and $N \geq 10$) the factor mainly determining the societal risks to road users is traffic density rather than tunnel design. In this region the risks are remarkably similar to those on the open road. The effect of tunnel design is seen, however, at the upper end of the spectrum ($N \geq 100$). This is illustrated by the following values of the ratio of the frequency for $N \geq 100$ to that for $N \geq 1$:

Tunnel 1	0.27
Tunnel 2	0.39
Tunnel 3	0.28
Tunnel 4	0.03

The low ratio for Tunnel 4 reflects the fact that it has a short length and a large cross-section, and the high value for Tunnel 2 reflects the fact that it carries two-way traffic and a small cross-section.

23.27 Pipeline Transport Hazard Assessment

A hazard assessment of a hydrocarbon pipeline is described in *A Safety Evaluation of the Proposed St. Fergus to Moss Morran Natural Gas Liquids and St. Fergus to Boddam Gas Pipelines* (HSE, 1978d).

The proposed natural gas liquids (NGL) pipeline would run for approximately 200 km from St Fergus to Moss Morran. The pipe would be 16 in. (406 mm) diameter and would operate at a maximum pressure of 1000 psig (70 bar) and a minimum pressure of 246 psig (18 bar) with a typical fluid temperature of 10°C. The pipeline would transport up to 110 000 bbl/d (approximately 100 kg/s). The composition of the NGL would vary between summer and winter conditions. For the former the NGL would contain approximately 50% ethane and 30% propane.

The failure rates of comparable pipelines and the factors influencing such failures are discussed in detail. The data considered include those of the US petroleum pipeline system, the European petroleum pipeline system and the UK gas transmission system, which have been described above. The report presents additional data on the UK petroleum pipeline system and on the UK gas transmission system.

The oil company pipeline system in the UK is only approximately 1500 miles long. In the period 1963–76 some 17 accidents were recorded. It was concluded that this is too small a number on which to base an estimate.

The data for the European petroleum pipeline system (CONCAWE, 1977 9/77) were analysed. Many of the types of incident recorded were considered inapplicable to the proposed pipeline. On the basis of applicable incidents the incident rate of the pipelines was 2.32×10^{-4}/km year.

The data for the UK gas pipeline system were provided by the British Gas Corporation (BGC). The applicable incident rate of the pipelines was again 2.32×10^{-4}/km year. This value was based on 31 faults. The distribution of rupture sizes of these faults was:

Table 23.48 *Hazards from the rupture of an NGL pipeline (Health and Safety Executive, 1978d) (Courtesy of the Health and Safety Executive)*

A Thermal radiation from burning vapours – distance from flame centre (m)

Release rate (kg/s)	*Radiation level* (kW/m^2)		
	1	8	16
20	128	45	32
100	282	100	70
250	450	160	112
1 000	892	315	223

B Quantity of vapour in concentrations above the lower flammability limit (LFL)[a]

Release rate (kg/s)	*Distance to LFL* (m)		*Carry time* (s)		*Mass above LFL* (kg)	
	D	*F*	*D*	*F*	*D*	*F*
50	200	800	40	400	2 000	20 000
100	320	1 300	64	650	6 400	65 000
250	510	2 400	102	1 200	25 500	300 000
1 000	1 100	6 100	220	3 050	220 000	800 000[b]

[a] Pasquill stability category D, wind speed 5 m/s; category F, wind speed 2 m/s.
[b] Limited by quantity in pipeline.

Equivalent diameter (mm)	*No. of faults*
> 80	1 (3%)
20–80	3 (10%)
< 20	27 (87%)

The hole sizes considered in the assessment were 80 and 20 mm equivalent diameters in the proportions 10% and 90%, respectively.

The emission rates from a rupture of the NGL pipeline were estimated as follows. Small orifices through which the maximum rate of emission as liquid would be less than 100 kg/s, the approximate maximum pump delivery rate, would release NGL as liquid. Orifices which could deliver more than 100 kg/s would give an initial liquid flow, followed by choked two-phase flow as the pressure fell locally to the saturated vapour pressure. At this lower flow the pressure would rise again and reversion to liquid flow would occur. There would follow an oscillation between liquid flow and two-phase flow. It was assumed for simplicity that the flow through this intermediate size of orifice would be 100 kg/s. The largest orifices would be able to deliver 100 kg/s or more with two-phase flow. For this latter case the flow under two-phase discharge was calculated as the geometric mean of the flows of pure liquid and pure gas. The flows calculated for the 20 and 80 mm holes were 15.2 and 100 kg/s, respectively.

These estimates were made for the first 5 minutes after the rupture. It was assumed that after this time the pumps would be shut off. The conditions after 5 minutes were not investigated, since it was considered that the leak would probably reach a critical phase in respect of ignition in less than 5 minutes.

The dispersion of the gas cloud from the pipeline was calculated assuming a neutral buoyancy gas and using the Pasquill equations. The effect of possible heavy gas behaviour was considered, but it was concluded that at the existing state of knowledge it is not unreasonable to assume that the increased entrainment of air approximately compensates for the slumping effect.

The heat radiated from a flame ignited at the pipeline was calculated by the methods given in API RP 521: 1969. The three heat radiation levels considered were 1, 8 and 16 kW/m^2. These were chosen because they are, respectively, the level which is just tolerable to a clothed person, that which would result in death within minutes unless adequate shelter were found and that which causes spontaneous ignition of wood. Some of the data given in the report for these hazards are shown in Table 23.48.

The frequency of 'interactions' between the pipeline and the exposed populations was assessed. The most exposed population group considered was that at Glenfarg, which is 250 m from the pipeline. For this population the frequency of interaction for all releases up to 100 kg/s was estimated as 4.4×10^{-5}/year. A further account of the approach taken in this work has been given by Bryce and Turner (1979).

Following a proposal to increase the diameter of this pipeline from 16 in. (406 mm) to 24 in. (610 mm), a reappraisal of the risks was undertaken (HSE, 1980c). Essentially the same methodology and data were used. The assessment found that the frequency of interactions remained highest for the population at Glenfarg. For this population the frequency of interactions for releases of 242 kg/s was estimated as 4×10^{-6}/year.

An treatment of the hazard assessment of pipelines from a broader perspective has been given by M.J. Turner (1980).

The hazard assessment of the British Gas pipeline in Morecambe Bay has been described by Considine (1983). The pipeline connects the offshore platform to the onshore terminal. It consists of a line about 40 km long and 36 in. diameter containing some 1774 te of gas and 612 te of liquid.

Scenarios for failure of the pipeline both on land and under water were considered. For the latter, there was uncertainty as to how the fluids released, particularly the liquid components, would behave. For the case of immediate ignition of the release, two scenarios were considered, one in which the release burns as a torch and the other in which it burns as a liquid pool on the surface with the gas confined to the area of the pool. For the case where the release does not ignite immediately, a gas cloud forms and drifts with the wind.

Consideration was also given to interaction with a passing ship. For this, three cases were envisaged: (1) the gas cloud drifts towards the vessel; (2) the vessel sails through the cloud; and (3) the vessel itself causes the release in some way such as by grounding or dragging its anchor.

23.28 Marine Transport Hazard Assessment

The mid-1970s saw a growing public awareness of the hazards from process installations and one manifestation of this was concern over ports and terminals, and the associated traffic, and in particular LNG terminals.

The US Coast Guard (USCG) initiated an extensive programme of work on the hazards of ships carrying hazardous materials. One outcome was the vulnerability model developed by Eisenberg, Lynch and Breeding (1975) and their co-workers, which is described in Chapter 9. Other work performed or sponsored by the USCG and other bodies includes that of Fortson *et al.* (1973), Woodward-Lundgren and Associates (1973), Dunn and Tullier (1974), A.D. Little (1974b), the National Materials Advisory Board (1974), Frenkel and Hathaway (1976), Stoehr *et al.* (1977) and the Planning Research Corp. (1979).

A scenario of particular concern was the spillage onto the sea of a large quantity of flammable liquid such as LNG or LPG. In the worst case such a spill could be massive and could be expected to spread and to vaporize rapidly, giving rise to a very large vapour cloud. There were similar concerns over liquefied toxic gases, particularly ammonia.

Treatments of, and models for, the spill hazard were described by Burgess, Murphy and Zabetakis (1970 BM RI 7448), McQueen *et al.* (1972), Fay (1973), Kneebone and Boyle (1973), Kneebone and Prew (1974), Drake and Reid (1977) and Hogan (1982). This hazard also figures strongly in the Vulnerability model.

The frequency of realization of such hazards, particularly that of collision, was dealt with in other studies such as those by Horner (1974), Horner and Ecosystems Inc. (1974), Kahn, Talbot and Woodward (1974) and Ligthart (1980).

At the same time studies were undertaken on particular projects, or project proposals, such as those for Staten Island, Los Angeles, Oxnard, Point Conception, Everett and Matagordo Bay. Studies include those by the Federal Power Commission (1974, 1976, 1977), Philipson (1974, 1980), Gratt and McGrath (1975a,b, 1976), Philipson and Schaefer (1975), Socio-Economic Systems (1977) and Nikodem (1978, 1980).

Accounts of the methodologies used in such work have been given by Philipson and Schaefer (1975), Kopecek (1977), Philipson (1978a,b, 1980), R.A. Cox, Comer *et al.* (1980), Lyon, Pyman and Slater (1982) and Philipson and Napadensky (1982).

More recent accounts of hazard assessments of particular terminals include those for Canvey (British Gas) by Lucas, Roe and Waterlow (1983), Kenai, Alaska, by Dale and Croce (1985), Mossmorran (Shell) by Sellers, Luck and Pantony (1985), St Fergus (British Gas) by Valk and Sylvester-Evans (1985), and an assessment by Bello, Romano and Dosi (1983).

Treatments of oil as opposed to LNG terminals are much less numerous. An example is that given by Bergmann and Riegel (1983) for the oil terminal at Galveston.

Aldwinkle and Slater (1983) have described the hazard assessment of a novel project, a process and storage ship (PASS).

More recent accounts of methodology include those of Valckenaers (1983), Valk and Sylvester-Evans (1985), Sellers and Luck (1986) and Navaz (1987).

The perspective of the HSE has been presented by Hough (1983), Wicks (1983), D.A. Jones (1985) and Crossthwaite (1986), while Considine and Grint (1985) have given a set of rapid assessment models, as described in Chapters 15–17.

23.28.1 Hazardous events

In marine transport, ships are at risk at the port approaches, in the port and during berthing, and whilst loading and unloading cargo. Accounts of scenarios of hazardous events during these different stages include the generic treatments by Solberg and Skramstad (1982), Hough (1983) and Cummings and Bradley (1988) as well as specific studies such as that of Lucas, Roe and Waterlow (1983). The studies by Aldwinckle and Slater (1983) on the PASS system and by Considine (1983) on the Morecambe Bay pipeline also contain relevant material.

The initial events fall into three broad categories: (1) release from cargo tanks, (2) release from a ship–shore transfer lines and (3) events associated with ship operations. The cargo which has been most studied is LNG and the following account refers primarily to this.

There are a number of events which have the potential to cause loss of containment of an LNG cargo. Two principal, and much studied, events are collision and grounding. Other events which have been examined as possible causes include: ship structural defects; liquid sloshing in a cargo tank; overpressurization of a cargo tank; a spillage on deck leading to brittle fracture; a fire on deck; a fire in a cargo tank; a fire on the sea; explosion in a cargo tank; an explosion in the engine room; and an explosion external to the vessel. Some of these rank as escalation events rather than initiating events.

A 125 000 m^3 gas carrier would typically have six 22 000 m^3 cargo tanks. The worst case scenario is a virtually instantaneous release of the ship's whole cargo of LNG, but this, whilst not physically impossible, is unrealistic. A more common, but still pessimistic assumption is a release from one cargo tank. More

detailed assessments consider the extent of damage from the initiating event under consideration, such as collision or grounding, and estimate the flow through the aperture thus created.

A detailed treatment of release flows and spill sizes is given Solberg and Skramstad (1982). The flow from a damaged cargo tank depends on the location of the hole. The authors present a graph for LNG showing the flow from different cargo tanks as a function of hole location, hole size and time.

The location of the hole also affects the total size of the spill. The largest spill size is given by a tank penetration at sea level. Solberg and Skramstad give another graph showing the fraction of the cargo which is released as function of the hole elevation.

A spill of LNG from a cargo tank may or may not be ignited immediately. Solberg and Skramstad mention as possible ignition sources in a collision: sparks; heating of steel above the methane ignition temperature due to absorption of collision energy; and ignition sources present in the bow of the striking ship.

For a spill onto the sea, if there is immediate ignition a large release will give rise to a pool fire. If the release does not ignite immediately, a large flammable cloud will form. If this cloud is then ignited, the combustion will take the form of either a flash fire or a vapour cloud explosion. Alternatively, LNG may be spilled within the double hull structure of the ship and ignited, resulting again in either fire or explosion.

Solberg and Skramstad suggest that a fire occurring in the double hull structure of the ship is likely to be starved of oxygen, unless the opening is very large and the spillage massive. For a pool fire on the sea beside the ship they give a detailed model, as described below.

This model indicates that, although a large pool fire will raise the temperature of both the outer hull and, after some delay, the inner hull, to a value at which some loss of strength will occur, this will not necessarily compromise the structural integrity of the whole ship. In this respect a spill which is relatively small but prolonged may present the greater threat. A much larger fire may be of too short duration to induce tank failure.

The creation of a flammable mixture in the double hull structure may result in an explosion. The hull contains void spaces interconnected by openings of different size. An explosion propagating through these voids could be very destructive. For a case where the whole space is filled by a mixture within the flammable range, Solberg and Skramstad estimate the explosion overpressure as of the order of 5–10 bar.

For a vapour cloud explosion over the sea outside the ship's hull they consider the effect of the overpressure at a distance of twice the radius from the centre of the cloud, which they take as about 0.1 bar. Treating the structural response as a quasi-static one, this overpressure is low compared with the strength of the hull and would not be expected to cause damage to the hull structure of the containment.

Another principal scenario for a massive spill is rupture of the ship–shore transfer system during loading or unloading. This event is considered by Lucas, Rowe and Waterlow (1983) and Cummings and Bradley (1988); the former authors also examine its escalation. Two possible causes of failure of the transfer system are failure of the expansion bellows and rupture of the transfer arm. A possible cause of transfer arm rupture is excessive movement between the ship and the jetty.

Estimates of the size of spill which could result from transfer system rupture is usually based on the full bore flow and the time to shut off the flow. Lucas, Rowe and Waterlow quote a transfer flow of 17 te/min and a response time to shut-down of 30 seconds or less.

These authors identify four ways in which, in principle, such a spill might escalate. If LNG is spilled on the deck of the ship, this may result in embrittlement and cracking of the steel. They conclude, however, that, given the low stresses, the cracks would arrest without extending beyond the embrittled zone.

The second way in which escalation might occur is the ignition of LNG spilled on the deck, giving a pool fire. The authors state that calculations of the heat transfer between the outer and inner hulls indicate that this would not cause inner hull failure or overpressurization of a cargo tank.

More serious is the third path to escalation, i.e. an explosion resulting from the entry of the liquefied gas into the ballast tanks. Lucas, Rowe and Waterlow describe the estimation of the resultant overpressure. In a totally confined enclosure the overpressure generated could be some 7 bar, which is well in excess of the pressure which most structures will withstand unless specifically designed to do so. However, commonly some weaker section fails and vents, thus reducing the pressure attained. Moreover, a high water level in the tanks tends to reduce the overpressure. The authors describe studies in which the overpressures calculated ranged from 0.07 bar for high water levels to 2 bar for nearly empty tanks, and other studies which indicated that in the absence of embrittlement by LNG such explosions would be unlikely to cause damage to the cargo tank.

The fourth path to escalation which these authors consider is an explosion in the engine room. In general no scenario for engine room explosion was identified which could cause cargo tank failure other than entry of a large quantity of flammable gas. For the latter case use was made of wind tunnel modelling and explosion simulation. It was concluded that in the worst case the peak overpressure in the engine room could be some 6 bar, which compares with a cargo tank failure pressure of 3–4 bar.

Events which may occur associated with operations on the ship are described by Cummings and Bradley (1988). They include (1) ignition of a vapour plume from a cargo tank, (2) improper control of ballasting/deballasting operations and (3) rollover of LNG in the cargo tank.

The foregoing account has dealt with LNG. LPG presents a broadly similar set of hazards. Some relevant differences are that it is not so deeply refrigerated and that it is more likely than methane to give a vapour cloud explosion.

Other materials may have their own characteristic hazards. Thus a monomer may undergo a runaway polymerization reaction. Monomers are stabilized using an inhibitor but Cummings and Bradley refer to work on the risk that delays at sea may cause the inhibitor to become exhausted.

23.28.2 Hazard models

As already mentioned, one of the first sets of hazard models for marine transport was the Vulnerability model (VM) of Eisenberg, Lynch and Breeding (1975) and other workers. This included constituent models for evaporation of pools on water, gas dispersion, pool fires, flash fires and vapour cloud explosions.

Another set of hazard models which has been applied to marine transport is that of Considine and Grint (1985). These authors present convenient parameterizations of a number of models widely used in hazard assessment, including models for heavy gas dispersion, pool fires, flash fires and vapour cloud explosions.

Whilst such sets of hazard models constitute a basic toolkit, other models also are required for hazard assessment. Treatments of collision and grounding have been described in Section 23.18.

Models are also required for the effect of fire outside the ship's hull on the integrity of the cargo tanks. Such models have been described by Solberg and Skramstad. The set of models given by these authors covers: the size and duration of a pool fire beside the hull as a function of the size of hole in the damaged cargo tank; the heat flux from such a fire as function of the fire base diameter; the heat flux received by the ship's deck; and the unsteady-state temperature profiles of the outer and inner hulls.

Another group of models is that for explosions in confined spaces such as between the inner and outer hulls and in ballast tanks. These include both models for the overpressures generated in a confined explosion and for the damage caused by such an explosion. The former may be analytical models or explosion simulation codes.

23.28.3 Some hazard assessments

As already described, there have been a considerable number of hazard assessments for marine transport, covering shipping, ports and terminals.

An early generic study was that given in the vulnerability model by Eisenberg, Lynch and Breeding (1975), as described in Chapters 16–18.

A hazard assessment of marine transport at an oil terminal at the Deep Water Port, Galveston, Texas, has been described by Bergmann and Riegel (1983). The scenarios considered were collisions and groundings, giving rise to a fire or explosion.

The authors' estimates of the frequencies and probabilities of these events are as follows. The frequencies of collision and grounding are estimated, respectively, as 1.5×10^{-4}/movement and 3.5×10^{-4}/movement, and the probabilities, given collision, of spill, fire and explosion as 0.25, 0.33 and 0.1. They give the following figures:

They take as negligible the probability that, given a soft bottom with no hard underwater object, a grounding would result in a spill or fire.

The authors found that for collisions only one in 23 spills resulting in fire propagated into an explosion, but that all explosions had resulted in spill and fire. Records indicate that where an explosion occurs, between 29% and 94% of the cargo tanks become involved, but that where a fire occurs some 10–13% of the cargo is spilled and burned. They take the proportion of cargo involved as 36% for an explosion and 12% for a fire.

Bergmann and Riegel have developed event trees for the three scenarios of collision, grounding and dockside fire/explosion. They assess the effects of explosion using the methods of W.E. Baker *et al.* (1978), including correlations of overpressure vs scaled distance for a fuel–air explosive and of damage in terms of the pressure–impulse diagram. For fire the treatment is largely concerned with fire fighting and mitigatory measures, and appears essentially qualitative.

The two C*anvey Reports*, described in Appendix 7, cover marine risks, including collision, grounding and loading/unloading, and give a full assessment of individual and societal risks.

A further hazard assessment of marine transport at the British Gas LNG terminal at Canvey is described by Lucas, Rowe and Waterlow (1983). This study details the various hazard scenarios, as described in Section 23.28.1, and gives an engineering assessment of each one. As a result of this assessment, some postulated scenarios are rejected, whilst others are accepted and countermeasures are described. For example, it is concluded that failure of the bellows expansion units in the ship–shore transfer line would be manifested by a small crack rather than sudden rupture, and that the latter is not a credible failure mechanism. Likewise, major failure due to low temperature brittle fracture following LNG spillage on the ship's deck is discounted. Further, a fire on deck or on the sea is not expected to cause failure or overpressure of the inner hull. On the other hand, the authors do consider to be credible explosions in the ballast space or, with ingress of flammable vapour, in the engine room. They describe various measures taken to counter these hazards such as improved emergency shut-down, deck protection and engine room explosion relief.

One countermeasure described is to arrange that in operation the man-way hatches to each ballast tank are closed, though not secured. This, it was calculated, would allow sufficient pressure to build up as the first LNG entering the tank vaporizes that further entry of LNG through cracks would be inhibited. This is an example of the exploitation of the characteristics of the initial event to prevent escalation.

Casualty type	*Frequency of casualty* (casualties/ movement)	*Probability of spill* (spills/ movement)	*Probability of fire* (fires/ movement)	*Probability of explosion* (explosions/ movement)
Collision	1.5×10^{-4}	4.3×10^{-5}	4.4×10^{-5}	1.6×10^{-5}
Dockside fire/ explosion	1.4×10^{-5}	9.8×10^{-7}	1.0×10^{-5}	3.7×10^{-6}

The authors comment that whilst a full quantitative risk assessment (QRA) has its place, in many instances most of the benefits may be obtained from the detailed engineering analysis which should in any case be part of a good QRA. It is often more fruitful to put effort into discovering unidentified problems rather than into quantifying those already identified. This should be done in co-operation with the engineers involved in the design and operation of the system.

The ACDS *Transport Hazard Report* gives a set of hazard assessments for specific ports and utilizes this to obtain an assessment of national societal risks.

23.29 Transport Hazard Assessment: Comparative Risks

There have been a number of hazard assessments which have sought to determine the relative risks of different modes of transport, of the transport of different chemicals, or of transport in different countries.

An early study of this nature was that of Westbrook (1974), described in Chapter 18, on the risks of chlorine transport by road, rail and pipeline.

Ormsby and Le (1988) give frequency–number (FN) curves for the transport of natural gas, gasoline, LPG chlorine and ammonia in the USA, and also make comparisons with other parts of the world. For LPG the dominant large event is the one that occurred at San Carlos. The study by Haastrup and Brockhoff (1990), described earlier, gives FN curves for transport in North America, Western Europe and other countries.

Sellers and Bendig (1989) have described a comparative study for transport by road and pipeline associated with two terminals.

The most comprehensive comparison of the risks of road vs rail is that given in the ACDS *Transport Hazard Report*. As described in Appendix 17, this study concludes that at least for the UK and for the four study substances there is no basis for preferring one of these modes of transport to the other.

23.30 Notation

Section 23.4

Section 23.4.7

A_0 fractional minimum elongation of metal on fracture under tensile stress
D internal diameter of shell (mm)
e thickness of metal (mm)
P calculation pressure (bar)
R_m minimum tensile strength
λ constant
σ permissible stress (N/mm^2)

Subscripts:
0 mild steel
1 metal under consideration

Section 23.4.12

d_{15} density of liquid at 15°C
d_{50} density of liquid at 50°C
DF degree of filling (%)
t_F mean temperature of liquid at time of filling (°C)
α mean coefficient of cubical expansion of liquid between 15°C and 50°C
χ parameter (%) (see text)

Section 23.5

C confidence limits on value of liquid density (%)
FR filling ratio
ρ_1 density of liquid
ρ_w density of water
χ parameter (see text)

Section 23.6

Equations 23.6.1–23.6.7

I normal distribution parameter
P probability
x impact speed
$\bar{x}$ mean impact speed
σ standard deviation

Superscript:
– mean

Subscript:
c combined

Equations 23.6.8–23.6.11

E energy absorbed in collision
m_1 mass of first vehicle
m_2 mass of second vehicle
v residual velocity of two vehicles after collision
v_l impact velocity of load
v_1 initial velocity of first vehicle
v_2 initial velocity of second vehicle

Subscript:
cr critical

Section 23.11

Equation 23.11.1

C cost
k constant
n index
P throughput

Equation 23.11.2

a design factor
D external diameter of pipe (mm)
f_y specified minimum yield strength (N/mm^2)
p internal design pressure above atmospheric (bar)
t design thickness of pipe wall (mm)

Section 23.18

c constant
E energy absorbed in collision
E_f energy absorbed by fender
K absorbed energy coefficient
L length of damage
m constant
m_1 effective mass of striking ship
m_2 effective mass of struck ship
δm hydrodynamic mass
P depth of damage
R ratio defined by Equation 23.18.6

R_T resistance factor
t thickness
v_{cr} critical value of speed of striking ship before collision
v_1 speed of striking ship before collision
V residual speed of two ships after collision

Subscripts:
cr critical value
n nth member in struck ship
N Nth member in striking ship
1 striking ship
2 struck ship

24 Emergency Planning

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Much of the foregoing material has been concerned with reducing the scale and frequency of hazards. Nevertheless, there remains for any hazard a finite possibility that it will be realized. It is necessary, therefore, to plan for such emergencies. Emergency planning is an integral and essential part of the safety and loss prevention strategy. Its objective is to mitigate the consequences of any incident which may occur.

The probability of the realization of a hazard is evaluated by a relatively sophisticated procedure, as already described. It is not then logical to assume that if this occurs the worst consequences will necessarily follow. It is more appropriate to take a probabilistic approach to the evaluation of the consequences also.

This point is well illustrated by the *Reactor Safety Study* of the Atomic Energy Commission (AEC, 1975), which has already been referred to in Chapter 9. In one particular scenario in that study the estimated number of early fatalities is reduced from 6200 to 350 if there is effective evacuation.

There is in fact plenty of practical experience to show the value of pre-planned and practised procedures for handling industrial emergencies, both in preventing an escalation of the original incident and in minimizing the exposure of people.

Planning for emergency situations is part of the general responsibility of the employer to protect both his employees and the public as embodied in the Health and Safety at Work etc. Act 1974 (HSWA). For major hazard sites it is an explicit requirement under the Control of Industrial Major Accident Hazards (CIMAH) Regulations 1984.

There are two main types of emergency with which the chemical industry is concerned. These are the works emergency and the transport emergency. They are somewhat different and require separate treatment. Whatever the type of emergency plan, the overall message is that it should be kept simple and flexible, but capable of being scaled up or down as circumstances demand.

Guidance on on-site emergency planning is contained in *Recommended Procedures for Handling Major Emergencies* (the CIA *Emergency Procedures Guide*) by the Chemical Industries Association (CIA) (1976/RC20) and *The Control of Industrial Major Accident Hazards Regulations 1984 (CIMAH): Further Guidance on Emergency Plans* (the HSE *Emergency Procedures Guidance*) by the Health and Safety Executive (HSE) (1985 HS(G) 25).

Guidance to the industry in respect of its responsibilities in relation to the off-site emergency plan is given in *Guidelines for Chemical Sites on Offsite Aspects of Emergency Procedures* (the CIA *Offsite Emergency Procedures Guidelines*) by the CIA (1984/RC20a) and in the HSE *Emergency Procedures Guidance*.

Selected references on emergency planning are given in Table 24.1.

24.1 Disasters and Disaster Planning

There is a considerable body of work on disasters of various kinds, both natural and man-made, and, whilst much of this may be only marginally relevant to process plant emergencies, it is helpful to have some awareness of this background.

Table 24.1 *Selected references on emergency planning*

Disaster planning
BSC (n.d./2); Prentiss (1951); Featherstone (1962); Ministry of Health (1962); Grosser *et al.* (1964); H.B. Williams (1964); Inbbar (1965); Healy (1969); Chatham-Savannah Defense Council (1971); Home Office (1972); Office of Emergency Preparedness (1972); Puget Sound Council of Governments (1975); J.W. Richardson (1975); W.H. Gibson (1976); J. Howard (1976); League of Red Cross Societies (1976); Manning (1976); Abe (1978); Quarantelli (1978); de Boer and Baillie (1980a,b); H.D. Foster (1980); Frey and Safar (1980); Smulders (1980); Whittow (1980); Geipel (1982, 1991); R. Jackson (1986); May and Williams (1986); Society of Industrial Emergency Services Officers (1986); Theodore, Reynolds and Taylor (1989); Dupont, Theodore and Reynolds (1991); M.A. Hughes (1991); D.J. Parker and Handmer (1992)

Works emergency planning
MCA (SG-4); NRC (Appendix 28 *Emergency Response, Emergency Planning*); Anon. (1961b); Labine (1961); Tenneco Oil Co. (1964b); Kling (1965); D.T. Smith (1967); Fowler and Spiegelman (1968); Gilmore (1968); Bennett (1972); van Cleve (1973); Hunter (1973); *Hydrocarbon Processing* Editors (1973); IRI (1973/9); PITB (1973/4); K. Wright (1973); Associated Octel (1974 Bklt 20/74); Brannon (1974, 1976); Bruce and Diggle (1974); Duff and Husband (1974); Maas (1974); CIA (1976 RC20, 1991 RC31, RC47); CISHC (1976/6); Diggle (1976); Underwood, Sourwine and Johnson (1976); Chlorine Institute (1977 FIRE, 1982 Pmphlt 64, 1985 OPFLOW); H.R. Hill, Bruce and Diggle (1977); Searson (1977); Webb (1977); API (1978 Publ. 2025); Harvey (1979b); Blanchard (1980); Melancon (1980); Willems (1980); Davenport (1981a); DnV (1981 RP C106); Isman (1981); Lihou (1981 LPB 42); E. Wilson (1981); Ranby and Hewitt (1982); G. Martin (1984); Burgoyne (1985c); HSE (1985 HS(G) 25); Husbands (1985); Lynskey (1985, 1985 LPB 61); Vervalin (1985a); IBC (1986/67, 1989/76); Marlier and Roure (1986); Walford (1986); Willcock (1986); CONCAWE (1987 11/87, 1988 6/88, 1989 2/89); Kalinins (1987); Mullins (1987 LPB 87); O'Reilly (1987); AIHA (1988–/13); Cassidy and Pantony (1988); ILO (1989); Kharbanda and Stallworthy (1989); Lakey (1998); ACGIH (1989/35); Marlier (1989); Tavel, Maraven and Taylor (1989); Phong (1990); AGA (1991/74, 75); Essery (1991); Ham and Gansevoort (1992); Keyworth, Smith and Archer (1992); Marsden, Ferrario and Green (1992); J.N. Scott (1992); Zika and Matyas (1992); Schulein, Kloet and Stolk (1993)
Off-site aspects: Quarantelli *et al.* (1979); Gabor and Griffiths (1980); J. Gray (1981); J. Gray and Quarantelli (1981); Tierney (1981, 1982); CIA (1984 RC20a); Quantarelli (1984); HSE (1986b); Bellamy and Harrison (1988); Cassidy and Pantony (1988); de Larderei (1988); NSW Government (1988); Pietersen (1988b, 1993); Egol (1989a); ILO (1989); Belanger (1990); J. Singh and McBride (1990); C.R. Young (1990); Essery (1991); Rogers and Sorenson (1991); Ruggiero, Macchi and Morici (1992); S. Wilson (1992, 1993); Callen, Dipema and Miller (1993); Thwaites (1993); Stephan (1994)

Evacuation: Hans and Sell (1974); Ikeda (1982) Lynskey (1985); Purdy and Davies (1985, 1985 LPB 65); Fitzgerald (1991 LPB 97); Essery (1993)
Gas dispersion hazards: Ryckman and Peters (1982); M.E. Smith *et al.* (1983); Purdy and Davies (1985, 1985 LPB 62, 63); McNaughton, Worley and Bodner (1987); Chikhliwader and Gelinas (1988); Ginnity (1988); Bais, Zerefos and Ziomas (1989); Rusch (1993); J.R. Taylor (1993)

Police
Drabek (1969); B.E. Fisher (1978a,b, 1980b); C.S. Lees (1985)

Fire services (see also Table 16.2)
Central Fire Brigades Advisory Council (1978); Gebhardt (1984); Beech (1985); Stephan (1994)

Medical services
Savage (1971, 1977, 1979); J.W. Richardson (1975); W.H. Rutherford (1975); Fozard (1976); Baskett and Zorab (1977); Easton (1977a,b); Lea (1977); Plewes and Hindle (1977); Snook (1977); Blanshan (1978); D.J. Williams (1979); de Boer and Baillie (1980a,b); Smulders (1980); Lessenger (1985); Thornley (1985)

Computer aids (see Table 29.1)

Transport emergencies
MCA (CC-1–CC-87); M.M. Anderson (1971); M.T. Miller (1971); Scannell (1971); Boardman (1972); Franklin (1972); Hess (1972); Benner (1975b); Cumberland and Hebden (1975); Ashton and Butcher (1976); McNeil (1976); Mesler (1976); BCGA (1977 GN1); Camm (1977); W.E. Clayton (1977); Mansfield (1977); Zajic and Himmelman (1978); Nimptsch (1979); Bosman (1980); Hart (1980); Somerville (1981); ASTM (1983 STP 825, 1990/1); Anon. (1984); Cooney (1985, 1991); Mascone (1986); O'Reilly (1987); Cashman (1988); CONCAWE (1988 5/88, 1989 7/89); Lakey (1988); Saccomanno and Allen (1988); Lycett *et al.* (1989); Rogers and Sorensen (1989); Quarantelli (1991); Sorensen, Carnes and Rogers (1992); Browne (1993); Stephan (1994)

Hazard information systems
Anon. (1986p); Cahill (1989 LPB 85)
Data sheets, Chem Cards: MCA (CC and CIC series); Bigelow (1970, 1971)
HAZCHEM: Home Office (n.d./6); London Fire Brigade (1973); Walmsley (1973); CIA (1975); FPA (1989 CFSD FS 6041)
TREMCARDS: CIA (n.d./2); Walmsley (1973, 1974)
National Chemical Emergency Centre: Cumberland (1978); Goodwin (1984); W.C.J. White (1985)

Emergency response
Road: IP (1989/1); API (1992 RP 1112)
Rail: Barron (1971); Cato and Dobbs (1971); O'Driscoll (1975a); A.D. Williams and Catalan (1976)
Pipeline: API (1991 RP 1122)
Sea: Sohnke (1971); Balemans (1975); H.D. Williams (1975); Preston (1983)
Fire services: Hayes (1971); F. Taylor (1975)

Emergency, mutual aid schemes
Gabor (1991)
HI scheme: Bigelow (1970, 1971); Sylvia (1972a, 1974); Anon. (1973a)
G Centres: ICI (n.d.a); Walmsley (1973)
CHEMSAFE: CIA (1973/6.1991 RC32); Moddrel (1977)
CHEMTREC: Bigelow (1970, 1971); Rosenhah and Cole (1973); Zercher (1975, 1976); Anon. (1994e); Resen (1986); E. Meyer (1989); Donahue (1994)
CHRIS: G.H. Brown (1976)
Chloraid: CIA (1983, 1992 RC48); Carr (1986)
CAER: Vervalin (1985b); Mascone (1986)

Particular chemicals
Ammonia: Cato and Dobbs (1971); Luddeke (1975); Greiner (1984); Lessenger (1985)
Chlorine: R.L. Mitchell (1971); Carr (1986); CIA (1992 RC48)
Missisauga incident: Whitaker (1980); Wignal and Leek (1980); Fordham (1982 LPB 44)
Hydrogen cyanide: Gemmill (1961b)
LPG: Anon. (1984v).
Vinyl chloride: Dowell (1971)
Glendora incident: Dowell (1971); Kogler (1971)
Radioactive materials: Lindell and Perry (1980)

Spectators
Hymes (1985 LPB 65)

Public relations, community impact, community response
Essex County Council (n.d.); MCA (SG-12); Segaloff (1961); D.T. Smith (1967); Horan (1970); Nesmith (1970); Vervalin (1970); CISHC (1976/6); Attwood (1977); Windscale Local Liaison Committee (1979); CIA (1980); J. Gray (1981); J. Gray and Quarantelli (1981); Preece (1982); Walker (1982); J. Harris (1985)

Aftermath
Geipel (1982, 1991)
Stress, including post-traumatic stress disorder: Weisaeth (1988, 1992); Gill and Picou (1991)
Land reclamation: SCI (1980); Pratt (1993)

Accounts of this work include *Emergency and Disaster Planning* (Healy, 1969), *Disaster Preparedness* (Office of Emergency Preparedness, 1972), *Disaster Technology* (Manning, 1976), *Disaster Planning* (H.D. Foster, 1980), *Types and Events of Disasters Organization in Various Disaster Situations* (Frey and Safar, 1980), *Disasters* (Whittow, 1980), *Disaster Policy Implementation* (May and Williams, 1986), *Accident and Emergency Management* (Theodore, Reynolds and Taylor, 1989) and *Hazard Management and Emergency Planning Perspectives in Britain* (D.J. Parker and Handmer, 1992).

In the UK the Disaster Prevention and Limitation Unit (DPLU) at the University of Bradford is a specialist resource on disasters. Another is the Disaster Research Center, Ohio State University, and latterly the University of Delaware in the USA.

For the process industries specifically, relevant material is *Highly Hazardous Spills and Emergency Planning* (Zadic and Himmelman, 1978), *Guide to Emergency*

Planning (Society of Industrial Emergency Services Officers, 1986) and *Emergency Response to Chemical Accidents* (O'Reilly, 1987).

24.2 Regulatory Requirements

For major hazard installations in the UK the CIMAH Regulations 1984 create a requirement for emergency planning, both on-site and off-site. Guidance on compliance is given in *A Guide to the Control of Industrial Major Accident Hazards Regulations* (the HSE *CIMAH Regulations Guide*) (HSE, 1990 HS(R) 21). Further guidance is given in the HSE *Emergency Procedures Guidance*.

Table 24.2 gives Regulations 10, 11 and 12 of these regulations. Regulation 10 places a duty to prepare an on-site emergency plan on the manufacturer and Regulation 11 places a duty to prepare an off-site emergency plan on the local authority, in consultation with the manufacturer. Regulation 12 requires the manufacturer to provide certain information to those who may be affected and to make that information publicly available.

Table 24.2 *Control of Industrial Major Accident Hazards Regulations 1984: Regulations 10, 11 and 12*

Regulation 10 Preparation of an on-site emergency plan by the manufacturer

(1) A manufacturer who has control of an industrial activity to which this Regulation applies shall, after consulting such persons as appear to him to be appropriate, prepare and keep up to date an adequate on-site emergency plan detailing how major accidents will be dealt with on the site on which the industrial activity is carried on and that plan shall include the name of the person who is responsible for safety on the site and the names of those who are authorised to take action in accordance with the plan in the case of an emergency.

(2) The manufacturer shall ensure that the emergency plan prepared in accordance with paragraph (1) takes into account any material changes made in the industrial activity and that every person on the site who is affected by the plan is informed of its relevant provisions.

Regulation 11 Preparation of an off-site emergency plan by the local authority

(1) It shall be the duty of the local authority, in whose area there is a site on which a manufacturer carries on an industrial activity to which this Regulation applies, to prepare and keep up to date an adequate off-site emergency plan detailing how emergencies relating to a possible major accident on that site will be dealt with and in preparing that plan the authority shall consult the manufacturer, the Executive and such other persons as appear to the authority to be appropriate.

(2) For the purpose of enabling the local authority to prepare the emergency plan required under paragraph (1), the manufacturer shall provide the authority with such information relating to the industrial activity under his control as the authority may reasonably require, including the nature, extent and likely effects off-site of possible major accidents and the authority shall provide the manufacturer with any information from the off-site emergency plan which relates to his duties under Regulation 10 or this paragraph.

Regulation 12 Information to the public

(1) It shall be the duty of a manufacturer who has control of an industrial activity to which this Regulation applies to –
(a) ensure that persons outside the site who are likely to be in an area in which, in the opinion of the Executive, they are liable to be affected by a major accident occurring at the site are supplied, in an appropriate manner, without their having to request it, with at least the information specified in Schedule 8 (which sets out the provisions of Annex VII to the Directive); and
(b) make that information publicly available.

(2) In preparing the information required to be supplied in accordance with paragraph (1), the manufacturer shall consult the local authority in whose area the industrial activity is situated and such other persons who seem to him to be appropriate, but the manufacturer shall remain responsible for the accuracy, completeness and form of the information so supplied.

(3) Without prejudice to his duty under paragraph (1), the manufacturer shall endeavour to enter into an agreement with the local authority in whose area the industrial activity is situated for that local authority to disseminate the information required to be supplied in accordance with that paragraph to the persons mentioned in it.

(4) The manufacturer shall ensure that the information supplied in accordance with paragraph (1) is updated and supplied again in accordance with that paragraph at appropriate intervals and made publicly available.

24.3 Emergency Scenarios

The basis of an emergency plan, whether on-site or off-site, is a suitable set of accident scenarios. It is important to select the scenarios at the right level of severity and for a suitable range of events.

Guidance on the level and range scenarios is given the HSE *Emergency Procedures Guidance.* This states: 'The emergency plan must be capable of dealing with the largest incidents that can reasonably be foreseen, but detailed planning should concentrate on those events that are most probable.' The range of events which may need to be considered may be wide, depending on the materials and activities on-site.

The on-site emergency plan should be flexible. There will normally be a basic plan covering a range of scenarios, with variations to adapt to a particular

scenario, which can be scaled up or scaled down, depending on the level of the incident. Similarly, it is normal for there to be a basic off-site emergency plan, but this plan also should be flexible and capable of being scaled up or down, as the case may require.

The HSE *Guidance* gives a classification of scenarios. For flammables, it distinguishes four types of event: (1) a fire with no threat of escalation, (2) a fire with a threat of escalation after some delay, (3) a fire with a threat of imminent escalation and (4) a sudden event. For toxics also, it distinguishes four types of event: (1) a slow leak, (2) a containment under threat, (3) a transient leak brought quickly under control and (4) a sudden massive release.

24.4 On-site Emergency Planning

As stated above, guidance on on-site emergency planning is given in the CIA *Emergency Procedures Guide* and the HSE *Emergency Procedures Guidance*. Accounts of on-site, or works, emergency planning are given by Bruce and Diggle (1974), Duff and Husband (1974), Lynskey (1985, 1985 LPB 61) and Essery (1991).

24.4.1 Definition of an emergency

The type of emergency considered here is the major emergency and it is this which is meant in all references to 'emergency' in this chapter. A major emergency in a works is one which has the potential to cause serious injury or loss of life and/or property and which tends to cause disruption inside and/or outside the works and to require the use of outside resources. Although it is usually the result of a fault on the installation itself, an emergency may also be caused by an external agency such as lightning, wind, floods, vehicle crashes or sabotage.

24.4.2 Identification and assessment of hazard

Emergency planning begins with the identification and assessment of the principal hazards. These will normally be the three major hazards: fire, explosion and toxic release. The identification stage may reveal a number of such hazards. These are then assessed to determine both the frequency of occurrence and the probabilities of consequences of various degrees of severity.

Duff and Husband (1974) have described the assessment of hazards of toxic releases for a major chemical works. They concluded that, although many chemicals were used on the site, in their case only three needed to be taken into account in emergency planning: ammonia, chlorine and hydrogen cyanide.

In this investigation potential sources of toxic material were listed as storage, tanker loading points, plant equipment and large inventory pipelines without isolation. Vulnerable points such as flanges, valves and pumps were noted. These high risk points were then mapped and possible emission rates and dispersion behaviour were estimated. From a study of the resulting scenarios some feel was gradually acquired for the probable nature and rate of escalation of emergency situations. It was recommended that this information should be recorded in a format which is usable in an emergency.

The identification and assessment of hazards has been dealt with in previous chapters, particularly Chapters 8, 9 and 16–18, and is not discussed further here.

24.4.3 Prevention of and protection against hazards

Emergency planning is undertaken at a point where it should be possible to assume that all proper measures have been taken to prevent and protect against hazards. Nevertheless, it is appropriate to consider emergency planning as an additional element in the hazard identification system to the extent that any hazard identified and assessed as significant is referred back to see whether it can be mitigated by additional measures.

Maas (1974) describes, for example, various measures suggested for installations where there is a large fire potential, including the use of rupture seams, overhead water tanks, fixed fire extinguishing equipment, etc.

24.4.4 Development of an emergency

A major emergency goes through three main stages: (1) raising of the alarm, (2) declaration of the emergency and (3) implementation of the emergency procedure.

Before considering works emergency planning it is convenient to consider the role of the external authorities and services.

24.5 External Authorities and Services

Major emergencies, and therefore plans for such emergencies, involve a number of outside authorities and services.

In the UK the reorganization of local government has greatly facilitated the development of rational emergency planning, giving comprehensive coverage over major industrial and transport complexes. An example is the emergency planning system for Teesside described by Bruce and Diggle (1974). Such unified authorities permit an emergency planning system which is much more effective than the former statutory requirements for co-operation between authorities.

At the level of major disaster planning, local authorities are encouraged to draw up Major Accident Plans. The scope of these plans is much wider than industrial emergencies alone, but management should be aware of such plans for their area.

In practice, industrial emergencies are handled mainly by the police and by the fire and medical services. It is important, therefore, to understand the role of each of these.

24.5.1 Police

The overall control of an emergency is assumed by the police. A senior police officer is designated as the Incident Controller. The police co-ordinate the activities of all the emergency services.

Formal statutory duties of the police relevant to an emergency include protecting life and property, controlling the movement of traffic and identifying the dead. There is a statutory duty to take charge of any incident where the general public is endangered.

Some important functions of the police in an emergency are the control of bystanders, the maintenance of access for essential traffic, the evacuation of the public from threatened areas, the identification of casualties, the informing of their relatives, the setting up of mortuaries and the investigation of suspected sabotage. They also liaise with medical services, such as hospitals and casualty clearing stations, and with the press.

One function which the police do not perform, and are in fact trained to refrain from, is rescue. This is the function of works rescue teams and of the fire services.

An account of the role of the police has been given by C.S. Lees (1985). He describes the police Major Incident Plan. The plan contains schedules of incidents which might occur, including those at chemical sites and transport emergencies involving chemicals. The author states:

> The Cleveland force is highly computerized, and each police station is equipped with computer terminals, VDU screens and fast printers giving immediate access to the force computer. In addition there is a message switching capability allowing instantaneous transmission to all terminals. Much of the initial action to be taken has been pre-planned and is contained in the computer allowing recall at the touch of a button.

The initial actions taken by the police include: ensuring that the fire and ambulance services are notified and given all available information; obtaining local weather information; mobilizing the police division; considering the need for road closures; dispatching a radio control car to the scene; activating a command base station; activating the force casualty bureau; and informing the local authority and thus activating their emergency plan.

Overall command is likely to lie initially with the divisional commander but to pass rapidly to the assistant chief constable. Police officers with delegated responsibilities during an emergency might typically include a communications officer, a personnel and welfare officer, a site property officer, a site transport officer and a press officer.

24.5.2 Fire services

The control of a fire is the responsibility of the Senior Fire Brigade Officer; this is his statutory duty under the Fire Services Act 1947. He also usually assists in and may take control of situations arising from other events such as explosions or toxic releases and of rescue work.

The fire service has a statutory obligation to maintain a fire brigade strong enough to meet all normal requirements, but this may not always be adequate to handle a major emergency on a chemical plant. However, a fire authority is also required to join in mutual reinforcement schemes with neighbouring authorities where these are practical.

The police and fire services should be given full information on the nature and scale of possible process emergencies and should devise plans to deal with these.

An account of the fire services in emergencies is given by Beech (1985).

24.5.3 Medical services

Hospital services are responsible for providing facilities for the urgent treatment of casualties. The capabilities of hospital casualty departments are somewhat variable. There has been a tendency, however, to reorganize these departments as Accident and Emergency departments. In some cases, particularly near motorways, a hospital may operate an emergency team which goes out to accidents.

Hospitals also should be fully informed of the possible process emergencies and should have appropriate plans. These plans should include not only the accommodation and treatment of the injured, but also their conveyance to hospital.

Accounts of medical services for emergencies are given in *Disaster Planning* (J.W. Richardson, 1975), *Red Cross Disaster Relief Handbook* (League of Red Cross Societies, 1976), *Rescue Emergency Care* (Easton, 1977b) and *Disasters: Medical Organization* (de Boer and Baillie, 1980b).

The emergency organization of ambulance services has been described by Smulders (1980) and Thornley (1985) and that of hospitals by Savage (1977) and de Boer and Baillie (1980a), who give detailed lists of duties.

24.5.4 Health and Safety Executive

The HSE will wish to be satisfied that an employer has undertaken appropriate formal and documented emergency planning, has acquired the necessary physical facilities, has worked out the procedures, has nominated and trained the personnel, and has established co-operation with the outside services.

Although it is sufficient to inform the local inspector of notifiable incidents after the event, he should be informed of a major emergency at once. He will then decide his own action.

In some cases, such as release of certain toxic gases, the inspector may be the only agency with the resources to conduct tests.

24.6 Works Emergency Plan

The essential elements in the Works Emergency Plan are:

(1) communication and control system;
(2) personnel with specified responsibilities;
(3) communication of the emergency;
(4) works emergency procedures;
(5) co-operation with outside services;
(6) public relations.

There should be an individual emergency planning document for each plant which may give rise to an emergency. This should outline the hazards and indicate how each is to be dealt with. It should describe the chain of command and communications, the procedures for rendering the plant conditions as safe as possible, for mobilizing the emergency services and for evacuation. Such a document ensures that a review has been made, gives a plan of action, makes clear the role of the emergency services and acts as a training manual.

24.7 Communications and Control System

Communication is a crucial factor in handling an emergency. When an incident occurs, it is necessary immediately to raise the alarm, to declare an emergency, to inform the works emergency services and threatened areas within the works and the outside services and threatened neighbouring areas. It is also necessary to contact relatives, press, etc. There will build up a large volume of two-way communications which may overload the system, unless this has been provided for.

24.7.1 Emergency Control Centre

An Emergency Control Centre should be provided. It should be located in a position of minimum risk and with good access both to the works and the outside road systems. It should also be accessible to the controllers who have to reach it to control the emergency.

The Emergency Control Centre must be able to function in an emergency and it must therefore not be disabled by the type of incident which may occur, e.g. fire, explosion or toxic release. If there is a toxic gas cloud hazard, it may be appropriate to design the centre so that it can function in the cloud, but it should be remembered that it is necessary for the controllers to be able to reach the centre initially and for other nominated personnel to go in and out during the emergency, and the situation where this has to be done through a toxic gas cloud should be avoided if possible.

The Emergency Control Centre should be linked by telephone to all essential points within the works and to the outside services. It is vital that this telephone system should function in the emergency. This means that there should be an adequate number of internal and external lines and that the electrical supply to the system should be secure, e.g. battery supplied. It is also necessary that the outside lines should not be neutralized by incoming calls and this may mean having at least one ex-directory number or one line capable of transmitting only outgoing calls.

The availability of mobile telephones provides a potentially powerful extension of the basic fixed telephone system.

The Emergency Control Centre should contain plans which facilitate control of the emergency. The list given in Table 24.3 follows broadly the listing given in the CIA *Emergency Procedures Guide*.

Any documentation required to administer the emergency should be provided. This will include the Works Emergency Plan and the list of nominated personnel.

There should also be lists of all personnel normally in the works, giving their department, assembly point, home address, nearest relative, and telephone number, if applicable.

Information from the hazard studies scenarios should be available in an appropriate format so that the Site Main Controller can carry out a continuous speculative review of the possible development of the emergency.

The Emergency Control Centre should be provided, as appropriate, with any equipment needed for dealing with the emergency, such as breathing apparatus, rescue gear, etc.

The Emergency Control Centre should be manned in an emergency by the Site Main Controller, nominated senior works personnel, senior officers of the outside services and any nominated assistants such as messengers. Other personnel should not be in the centre. If the hazard justifies it, the Emergency Control Centre may be manned continuously.

On large sites, or where there is a major toxic hazard, consideration should be given to the provision of a second control centre, as a back-up in case for any reason the main Emergency Control Centre cannot be used.

Table 24.3 *Some plans required in the Emergency Control Centre*

There should be plans which indicate:
Large inventories of hazardous materials
Radioactive sources
Fire water system and alternative water supplies
Other fire fighting equipment
Safety equipment
Works entrances and road system
Assembly points, refuge rooms
Relation of works to immediate surroundings
and plans which can be used as an emergency develops to show:
Areas affected by hazard
Areas evacuated
Deployment of emergency teams and equipment

24.7.2 Alarm systems

As the emergency develops, it may be necessary to communicate to personnel dispersed over the works (1) the raising of the alarm, (2) the declaration of the emergency and (3) the implementation of on-site evacuation.

The system for raising the alarm should have a sufficient number of readily accessible and identifiable points from which the alarm can be raised. This may be done directly or indirectly, e.g. by communication to the Emergency Control Centre. The alarm signal should be receivable in all parts of the works. While the signal may usually be a local audible signal, difficulties can arise in noisy areas or in areas outside buildings. In such cases it may be necessary to install more numerous audible signals or to use visual signals, e.g. flashing lights.

It is not desirable to utilize too many different types of alarm. There is some consensus that two types are enough, one for fire/explosion and one for toxic release.

If an emergency is declared, personnel in the works may be informed by the use either of the above alarm system or of a separate emergency alarm system. The latter is unusual and the ordinary works alarm system is normally used. Thus the declaration of the emergency may be signalled by sounding the alarm in a different way, e.g. over a longer time period.

Finally, it is necessary to have a system which signals the implementation of evacuation procedures. Again a separate evacuation alarm system may be provided. Alternatively, use may be made of the existing alarm system.

It will be apparent that the alarm system does constitute a problem, arising from the requirement to signal separate stages of the emergency, the undesirability of a proliferation of alarm systems, and the need to keep signals clear and unambiguous.

An account of a particular works alarm system has been given by Lynskey (1985). He discusses in particular the relative merits of a siren and of public address system. The method adopted was a siren, on account of its better audibility. But, subsequently, minor emergency systems were built up based on the greater versatility of the public address system. He also gives details of the testing of alarm systems.

24.7.3 Mobile telephones

Current guidance on emergency planning makes little reference to the use of mobile telephones. These clearly have a role to play, although they are relatively expensive. The guidance given here largely retains the emphasis on fixed telephone systems. If mobile telephones are used, some modification is in order, but the essential principles still apply.

24.8 Essential Functions and Nominated Personnel

24.8.1 Works Incident Controller

A Works Incident Controller should be appointed. It is his function to proceed to the scene of the incident and to take control of it. A full list of his duties is given in the CIA *Emergency Procedures Guide*. The list given in the HSE *Emergency Procedures Guide*, which is essentially similar but up-dated, is given in Table 24.4.

The CIA terminology for this post is retained here in preference to the HSE terminology, which is simply Incident Controller, in order to avoid confusion with the police Incident Controller.

The declaration of the emergency is a normal function of the Works Incident Controller, although, as described below, authority to declare it is not restricted to him.

Table 24.4 *Responsibilities of the Works Incident Controller (Health and Safety Executive, 1985 HS(G) 25) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

(a) As soon as he has been made aware of an incident the Incident Controller should assess its scale against predetermined criteria or emergency reference levels, and decide whether a major emergency exists or is likely. If so he should immediately activate the on-site plan and if necessary the off-site emergency plan (see paragraphs 47 to 50)[a].

(b) He should assume the duties of the Site Main Controller pending the latter's arrival, in particular to:
  (i) ensure the emergency services have been called;
  (ii) direct the shutting down and evacuation of the other plant areas, etc., likely to be affected;
  (iii) ensure key personnel have been summoned.

(c) His main function, however, is to direct all operations at the scene of the incident, e.g.:
  (i) rescue and firefighting operations, until the arrival of the fire brigade, when he should hand over control to a senior fire officer;
  (ii) search for casualties;
  (iii) evacuation of non-essential workers to assembly areas.

(d) He should also:
  (i) set up a communications point with radio, telephone or messenger contact with the Emergency Control Centre;
  (ii) give advice and information as requested to the emergency services;
  (iii) brief the Site Main Controller and keep him informed of developments.

[a] Reference is to HS(G) 25.

Table 24.5 *Responsibilities of the Site Main Controller (Health and Safety Executive, 1985 HS(G) 25) (Courtesy of HM Stationery Office. Copyright. All rights reserved)*

(a) The Site Main Controller should go to the Emergency Control Centre and take over from the Incident Controller responsibility for overall control.

(b) If he decides that a major emergency exists or is likely, he should ensure that the emergency services have been called and the off-site plan activated.

(c) Depending on the circumstances, he should then:
  (i) ensure that key personnel are called in;
  (ii) exercise direct operational control of those parts of the works outside the affected area;
  (iii) continually review and assess possible developments to determine the most probable course of events;
  (iv) direct the shutting down of plants and their evacuation in consultation with the Incident Controller and key personnel;
  (v) ensure that casualties are receiving adequate attention. Arrange for additional help if required. Ensure that relatives are informed;
  (vi) in the case of emergencies which involve risk to outside areas from wind blown materials, contact the local meteorological office to receive early notification of impending changes in weather conditions;
  (vii) liaise with chief officers of the fire and police services and with the Health and Safety. Executive; provide advice on possible effects on areas outside the works; ensure that personnel are accounted for;
  (viii) control traffic movement within the works;
  (ix) arrange for a log of the emergency to be maintained;
  (x) where the emergency is prolonged, arrange for the relief of site personnel and the provision of catering facilities;
  (xi) issue authorized statements to the news media;
  (xii) ensure that proper consideration is given to the preservation of evidence;
  (xiii) control rehabilitation of affected areas after the emergency.

Where a fire is involved, the Works Incident Controller will direct fire fighting until the outside Fire Services arrive, but he will then hand over control of this aspect to the senior officer of the fire brigade.

The Works Incident Controller should be thoroughly familiar with the works situation; a suitable person is the shift section manager.

It is important that the Works Incident Controller be readily recognizable when he is at the scene of the incident. This is facilitated if he wears a distinctive garment such as a brightly coloured or luminous jacket or helmet. This garment should be known to all concerned and should be distinct from any which might be worn by others at the scene, including the outside services.

Table 24.6 *Some functions frequently required in an emergency*

Plant control/shut-down
Leak control
Fire fighting
Hazard reduction (removal of tankers, etc.)
Movement of equipment (fire fighting, first aid equipment, etc.)
Chemical analysis (toxic, radioactive materials, etc.)
Engineering activities (repair of plant, utilities, etc.)
Traffic control (at incident, within works, at works entrance, etc.)
Evacuation (manning of assembly points, accounting for works personnel, handling contractors and visitors)
Rescue
First aid and casualty clearance
Communications inside works (messengers)
Communications outside works

24.8.2 Site Main Controller

A Site Main Controller should also be appointed. His function is to go to the Emergency Control Centre and to take overall control of the emergency in the works. A full list of his duties is given in the CIA *Emergency Procedures Guide*. The list given in the HSE *Emergency Procedures Guide*, which is essentially similar but updated, is given in Table 24.5.

The Site Main Controller should be familiar with the works situation and should have the authority needed to take any necessary major decisions affecting the works, the neighbourhood and the outside services. A suitable person is the shift works manager.

For both controllers deputies should be appointed who can take over their duties if they are unavailable for any reason.

24.8.3 Other functions and personnel

There are numerous other functions which may have to be carried out in an emergency. Some of these functions are normal, though they can easily become overtaxed in an emergency, but most are specific to the emergency situation.

A list of some of these functions is given in Table 24.6; other lists are given by D.T. Smith (1967) and in the CIA *Emergency Procedures Guide*. Personnel should be nominated for all these essential functions. These personnel effectively constitute a Works Emergency Team.

24.9 Declaration and Communication of the Emergency

24.9.1 Raising the alarm

When a serious incident occurs, it is very desirable for the alarm to be raised as quickly as possible. Prompt action will in many cases forestall the development of a full emergency.

Crucial aspects of raising the alarm are the authority to raise the alarm, the training of personnel, and the alarm system. An efficient and widely practised policy is to allow any employee to raise the alarm. Such a policy is more effective if personnel have been specifically trained in this aspect.

Table 24.7 *Some parties who may have to be informed of an emergency*

Personnel on the plant concerned
Personnel on other threatened plants
Personnel throughout the works
Key works personnel on call-in
Police
Fire services
Medical services
Neighbouring firms
Press
Head office

24.9.2 Declaration of the emergency

When the alarm has been raised, the Works Emergency Procedure is activated. The first stage of this is the decision as to whether the incident constitutes, or could develop into, an emergency. The Works Incident Controller should go to the scene of the incident. He then makes the decision whether to declare an emergency.

The authority to declare an emergency need not be restricted to the Works Incident Controller, however. It is undesirable, of course, to allow the authority to be too widespread, but too close a restriction may introduce an undesirable delay into the declaration. Other competent personnel may therefore be vested with this authority.

24.9.3 Communication of the emergency

Once an emergency has been declared, it must be communicated to the Site Main Controller, to personnel working within the works, to works personnel to be called in from outside, to the outside emergency services and to others. Some of the parties who may need to be informed are listed in Table 24.7.

As far as possible the Works Incident Controller should be relieved of the task of communicating the emergency so that he can devote his efforts to dealing with it on site. However, the duties listed in Table 24.4 do include communication of the emergency to interested parties until the Site Main Controller arrives. It may be appropriate to consider arrangements which assist the Works Incident Controller in this task.

It is desirable to work out in advance fairly formal procedures for the notification of an emergency. The order in which the different parties are to be notified is one obvious aspect. It is also necessary to avoid entering into lengthy explanations to personnel on call-in and here use may be made of short pre-arranged messages. Personnel liable to call-in should be issued with identification which will allow them to pass through police barriers erected to control traffic and sightseers.

It is essential that the existence of an emergency be notified without delay to affected plants within the works, the Works Emergency Team and the outside services.

The emergency should be notified to any neighbouring firm which might be affected by it. This may be necessary if there is a threat to the firm's plant or personnel, if the firm's activities could compound the emergency, e.g. create a traffic jam at a shift change, or if there are mutual assistance arrangements.

24.10 Works Emergency Procedures

24.10.1 Action on declaration of emergency

The action to be taken by all personnel on the declaration of an emergency should be worked out and personnel should be trained in it. This action may include procedures which obviate the alarm problem, as described earlier. Thus the CIA recommendations suggest that as an alternative to the use of a second and separate emergency alarm the initial alarm may be raised over the whole works and that the following procedure is then implemented:

(1) All members of the workforce return to their normal place of work, provided it is safe to do so.
(2) Personnel who are in charge of plants and departments and who are nominated to other duties go to their offices to await instructions from the Emergency Control Centre.
(3) Senior managers nominated as key personnel go to the Emergency Control Centre from which, acting on the advice of the Works Incident Controller, they issue instructions.

24.10.2 Evacuation of personnel

When an emergency occurs, it is usually necessary to evacuate from the affected area all personnel not directly involved in dealing with the incident. It may also be desirable to evacuate non-essential personnel from adjacent areas which could be affected if the incident were to escalate.

On evacuation people should go to pre-assigned assembly points which should be located in a safe place. More than one assembly point is necessary, because people should not have to go near the affected area to reach the point and because a particular point may be downwind of the hazard, e.g. fire or toxic release.

An assembly point should be clearly marked with a conspicuous notice and an identification number or letter. It should have telephone communication with the Emergency Control Centre.

Each assembly point should be manned by a nominated person. It is his duty to record the names of those reaching the point and to keep in communication with the Site Main Controller in order to help locate missing personnel and to receive further instructions on evacuation.

Accounting for personnel is a major problem, because it is difficult to know precisely who is in the works at a given time, especially if contractors are on site or if there is a shift change. It is usually considered impractical to maintain a list of personnel updated on a daily basis and instead the lists kept are nominal ones which are updated informally when the emergency occurs. There should also be lists of contractors' personnel and of visitors.

24.10.3 Refuge rooms

It may be necessary to provide shelter at the assembly point, i.e. a refuge room, particularly if there are toxic hazards. The design of such rooms is discussed by Duff and Husband (1974). The size required is generally underestimated, the limiting factor usually being body heat and humidity rather than oxygen for breathing or carbon dioxide exhaled. The room should contain breathing apparatus. A more detailed account of refuge rooms is given in Chapter 10 in the context of plant layout.

Refuge rooms play an important role in the emergency plan for a site with large chlorine storage described by Lynskey (1985). Initially draft plans relied heavily on observing the wind direction and moving people to open assembly areas upwind or far enough across wind to be safe. In the event, the geography of the site precluded this, and a system of refuge buildings was adopted.

Industrial buildings tend to have quite high ventilation rates, and in order to make such a building suitable as a refuge against toxic gas it is necessary to ensure that there is a reduced ventilation rate. The refuges are marked with a prominent 'Toxic Gas Refuge Area' sign.

Lynskey also considers the arrangements required to ensure that personnel make their way to the refuge area. Staff are instructed that if they are aware of a chlorine escape they should observe the wind direction and go to the nearest safe refuge. Emergency escape respirators of the half mask or 'grip in the mouth' type are provided. In accordance with the system described above, each refuge has a marshall, who is responsible for the roll call, and a deputy marshall.

24.11 Co-operative Planning, Training and Exercises

24.11.1 Planned co-operation with external services

The planning of co-operation and the development of understanding with the outside services is vital to good emergency planning. The first step is obviously agreement to co-operate by the senior managers of the organizations involved. But this needs to be followed up by active planning and exercises by their subordinates.

Action by industry and by the local authority should be seen not as two disjoint activities, but as a single operation in which a growing weight of resources is brought to bear on the incident. The planning should aim to clarify not only what is to be done but who is to do it.

Co-operation benefits greatly if there is a full-time liaison officer, and this can be justified in an area where there is large potential for emergencies. Bruce and Diggle (1974) state that the Teesside Fire Brigade employs an Industrial Liaison Officer.

What is known in advance is the general location and nature of possible emergencies. Other factors will not be so well defined: time, weather, numbers of people. Excessive detail in the planning should be avoided. The aim should be to plan broad areas of responsibility, chains of command and systems of communication.

At the level of hardware, compatibility of equipment is important, so that situations are avoided where the fire brigade cannot use the works water supply or works stretchers cannot be fitted into the public ambulances.

The outside services will require their own communications. On-site the practice has been for the police, fire and medical services to be linked by radio to their own communications systems. The Emergency Control Centre should be available to them. Alternatively, they

may wish to set up their own mobile control centres. The use of mobile telephones may result in some modification of this basic system.

These services will also normally need to tap into the works internal communications. Again they can do this through the Emergency Control Centre. An alternative is to provide for their use portable radios as used in the works.

Each service should have its own emergency plans. The Teesside system described by Bruce and Diggle (1974) illustrates a well developed system of emergency planning. The police have a Major Incident Plan which covers road, rail, aircraft and airports as well as industrial situations. This includes a Hospital Major Accident Organization. The fire service has a number of emergency plans.

In addition, if the emergency should escalate to very serious proportions, there is within the local authority a Co-ordination Scheme administered at a high level which can make available the resources of such departments as the Borough Engineer, Education (for shelter in schools), Transport, Social Services, etc.

Co-operation in planning is supplemented by activity in communications. If there is a fire in the works, the fire brigade is alerted. If there is a flammable gas or toxic release, the police come in. In this way the communications system is kept active.

24.11.2 Training for emergencies

It is important for all employees to be thoroughly trained in emergency procedures. This includes: recognition of alarm signals (initial alarm, emergency, evacuation); conduct of specific functions and use of specific equipment (see Table 24.6); and personal action on instruction to evacuate.

Personnel in the outside services are trained in their job already, but may benefit from additional training relevant to industrial accidents, including familiarization with particular equipment and industrial sites.

Visitors and contractors should be told what to do in an emergency.

24.11.3 Exercises for emergencies

Emergency exercises are effective in familiarizing personnel with their functions. Duff and Husband (1974) describe exercises for emergencies (minor emergencies) and disasters (major emergencies). They state that an interval of 2 months is used for the former and that in addition several real emergencies can be expected each year. The interval between exercises for disasters is 3 months and, of course, these are rare events. Both types of exercise involve works personnel generally, while the latter also includes table top exercises for the Disaster Control Team.

Fire fighting exercises are described by Bruce and Diggle (1974). Five-pump exercises are held every 2 months and 10/20 pump exercises every 6 months. The exercises are thus fairly large, but this is necessary; small exercises are not sufficient.

A prime aim of such exercises is the development of mutual understanding and respect between the works personnel and the outside services. This may prove of great value during the stress of a real emergency.

24.12 Public Relations

If a major incident occurs, to give no report in the press is not an option open to a company. The choice is between an attitude to the press which may foster informed and sympathetic reporting and one which almost guarantees ignorant and hostile comment. A company is unwise to expect sympathetic reporting unless over the long term it has built up with the press, as far as it is able, a relationship of trust based on openness about the hazards present and the preventive and protective measures adopted. It will normally be appropriate that the long-term handling of major hazard policies be done by the company's head office with reference to national policies and standards.

In this connection the distinction drawn by Vervalin (1970) between the role of the editor and that of the reporter may be borne in mind. He defines the function of the editor as that of getting questions answered by authoritative and qualified persons.

The reporter's job, of course, is to get a story and the photographer's is to get pictures. The questions which the reporter wishes to have answered in the first instance are essentially what happened, where, when and how it occurred, what casualties and damage there have been, and whether the incident is under control or not (Horan, 1970).

It is in the company's interest to take the initiative in issuing the news of an emergency and in providing what information it can. This will reduce the likelihood of erroneous reports, the effect of which may not be easy to repair. Reporters also need the physical facilities of a press room with outside telephones and access to the company spokesman.

A senior manager should normally be appointed as the sole authoritative source of information. Other employees should be instructed not to comment themselves but to refer inquiries to this spokesman. This senior manager may be assisted by the professional press officer, who is more experienced in dealing with the press and is aware of the reporter's problems of communications and deadlines.

It is important to avoid simply stone-walling reporters. Describing the reporter's viewpoint, Nesmith (1970) comments that he is almost always able to obtain a story from the people directly involved, but rarely through appointed intermediaries.

Some further practical aspects of relations with the press are described by Lynskey (1985) in the context of practices of the emergency plan. He states that this is an area which initially was grossly underestimated. Reporters are quite likely to arrive with the first wave of the fire services. They will not be prepared to await a managerial conference. There needs to be a senior person there to deal with them, summoned in the first call-out list.

Media inquiries can put a serious load on the emergency control staff unless specific arrangements are made to prevent this.

In some circumstances the local radio may have a role to play in broadcasting advice to residents on the situation and on the action to be taken.

24.13 Practical Implementation

The effectiveness of the emergency system in a real emergency depends critically on the extent to which it has been thoroughly practised. An account of this aspect has been given by Lynskey (1985). After describing features of an emergency plan for a site where the main hazard is liquid chlorine, Lynskey comments:

> At this stage of development there was a superficially effective system. Well labelled refuge areas, stocks of respirators, an effective warning system and communication equipment represented a substantial investment in the system. The procedure was fully documented and circulated to all function holders. Notices around the site and a handout to all staff ensured that the evacuation procedure was fully circulated. Looking back at that stage there was a great sense of achievement. However, at that stage the procedure was rather analogous to a learner driver who knows all the correct actions but has yet to develop reflexes.

In contrast to procedures for normal operations, emergency procedures do not benefit from being regularly practised in the real situation. It is necessary, therefore, to practice them by conducting exercises. These serve two purposes: to identify and remedy weaknesses and to give personnel confidence in the procedures.

Lynskey describes the use of a variety of methods of practising the emergency plan. Practice evacuations were conducted of a separate section to single refuge, leaving a skeleton crew where necessary. A whole works evacuation was also practised by evacuating the incoming shift whilst holding back the outgoing one. The roll call at a refuge was also practised between the refuge marshall and the central control.

For the training of the controllers use was made of table top exercises. The developing scenario was presented as a series of observed events which the controllers had to interpret. A major aspect of the exercises was simulated communication with personnel to be called out, the emergency services, anxious relatives and the press. Personnel clearly found the simulations realistic and were deeply involved, as evidenced by a hesitation before declaring an emergency.

These practices revealed a number of misconceptions and deficiencies. It had been assumed initially that the external fire brigade should be told first the wind direction and speed, whereas their initial concern was to be given a safe route to the site. Similarly, it was assumed that the fire brigade would start by setting up water curtains, whereas their first priority was in fact search and rescue.

The roll calls by the marshalls at the refuges went badly at first. Returns were made rapidly but were found to be defective. Practice of this aspect led to considerable improvement.

It was found that assumptions had been made about personal skills which were unfounded. In one case a nurse was assigned to drive a vehicle but was not a qualified driver.

Emergency training is a potentially large training commitment, especially for contractors' personnel such as engineering contractors and contract services. Use was made of tape–slide presentations.

Another aspect on which much was learned was relations with the press, as already described.

Further lessons from practices are described by Essery (1991). 'Table top' exercises can be conducted in quite a short time and thus allow a number of different scenarios to be simulated. Rather more realistic are 'control post' exercises in which personnel are called in and fed information much as they would receive it in a real situation.

Many of the lessons learned relate to communication. Messages may be passed on without understanding; they may be understood in one part of the organization but not in another; they may be interpreted in different ways.

24.14 Real-time Aids

Advances in the modelling of hazardous releases and their consequences offer the potential for the use of such models in real time as aids during an emergency. The use of such models is discussed by Essery (1991), who concludes that since fires and explosions tend to develop rapidly and in a wide variety of ways, the application of models for these is likely to be fairly limited, but that there is more scope for models of gas dispersion, particularly for toxic gas. This does in fact seem to be the direction in which real-time aids are moving.

24.14.1 Gas dispersion

A number of accounts have been given of aids for the modelling of gas dispersion in real time, so that the development of the gas cloud can be predicted and appropriate action taken.

Lynskey (1985) has described the use of a pre-calculated chart for the dispersion of a chlorine gas cloud, showing the distance to a concentration of 15 ppm vs release rate in Pasquill stability category D conditions with wind speed as parameter. The chart has marked on it the release rates typical of particular leak scenarios such as a tanker filling line or a line to a vaporizer.

The use in real time of a computer program for gas dispersion is described by Essery (1991). In a practical situation, it is unlikely that the actual release rate would be known with any accuracy. But it may be possible by taking field measurements and using the gas dispersion model to work back to obtain an estimate of the release rate and then to predict forward the further development of the cloud.

The gas cloud may well be moving at quite a high speed, say 5 m/s, so that the time available in which not only to make gas dispersion estimates but also to take action based on them may be short, depending on the action envisaged.

24.14.2 Resultant action

There is a dearth of information published by operators both on the precise way in which such aids are intended to be used as an aid to action and on their use in real emergencies.

24.15 Computer Aids

There are two principal types of aid developed for use in emergency planning. One is computer-based simulation of emergencies for use in emergency training and in emergency exercises. An aid of this kind has been

developed by the Institution of Chemical Engineers (IChemE).

The other type of aid provides a simulation in real time of physical phenomena such as gas dispersion. The SAFER system and it successors is perhaps the best known system of this kind.

An account of both types of computer aid is given in Chapter 29.

24.16 Off-site Emergency Planning

As stated above, in the UK Regulation 11 of the CIMAH Regulations 1984 requires the local authority to prepare on off-site emergency plan. Guidance on off-site emergency planning is given in the CIA *Offsite Emergency Procedures Guidelines* and the HSE *Emergency Procedures Guidance*. The guide *Emergency Plans for Civil Nuclear Installations* (HSE, 1986b) also contains information which may be useful to local authorities.

24.16.1 Local authority disaster planning

In the UK, planning for emergencies has long been the responsibility of local authorities. The need for emergency plans has been stimulated by the creation of statutory obligations on emergency services rather than requirements for emergency plans as such. The development of emergency plans was encouraged by Home Office Circular ES 7/1975 *Major Accidents and Natural Disasters*.

District councils deal with emergencies within their boundaries backed up by county, regional or metropolitan councils, as the case may be. County councils maintain plans which go by various names such as Major Accident Plan.

The CIMAH Regulations require the county council to have a major accident plan for specific CIMAH sites. This plan will generally build on the existing major accident plan, but adds to it additional site-specific features.

The action to be taken by the local authorities and the operator is summarized in the CIA *Offsite Emergency Procedures Guidelines*.

24.16.2 Joint action by local authority and operator

The local authority (LA) and the operator should co-operate in formulating a set of suitable, credible accident scenarios on which the emergency plan can be based. These should involve realistic rather than maximal accidents.

There should be established between the LA and the operator a communication system capable of handling an emergency without delay and confusion and a system of recognized alarm procedures to alert the emergency services both on and off site.

The two parties should together provide information to neighbouring companies whose sites may be affected by an incident, to the HSE and to the media.

They should make arrangements for a post-incident analysis to determine whether any changes to the emergency plan are called for.

24.16.3 Action by operator

The operator should brief the emergency services on: the materials handled on site and their hazards; the nature of the installations involved; and any particular hazards and precautions relevant to the incident. It should assess the effect of the incident on neighbouring sites, and take any appropriate action. It should make available experts who can provide specialist advice, and be prepared to deploy trained people, including persons from other sites, if the situation warrants it.

24.16.4 Action by local authority

The local authority for its part should nominate the person(s) responsible for its emergency plan and create a chain of command for implementing it.

It should assess the requirements for emergency equipment of various kinds and ensure that these are available. These should include the equipment for the communication links, including telephone and radio, and for fire fighting.

It should prepare plans for the control of road traffic, rail movements and port, marine and air activities, and for the discouragement of sightseers.

It should formulate criteria for deciding on the advice to be given to local residents, and in particular on the decision as to whether to evacuate or to remain indoors.

It should also formulate criteria for deciding that the emergency is over and arrangements for signalling the all-clear.

24.16.5 US system

In the USA there are developing requirements for off-site emergency planning, as described in Chapter 3. Off-site emergency planning comes within the Community Awareness and Emergency Response (CAER) programme, launched in 1985 under the aegis of the Chemical Manufacturers Association (CMA). This programme seeks to ensure that on-site emergency plans, which generally were already in existence, are co-ordinated with the off-site plans of the local community. Guidance is given in the CMA *CAER Manual*. Accounts of the CAER programme are given by Vervalin (1985b) and Mascone (1986).

24.17 Provision of Information

The CIMAH Regulations 1984, in Regulation 12, place on the manufacturer the duty of provision of information to the public. The manufacturer is required to consult the local authority on this matter and to seek to enter into an agreement with it so that the information is supplied by the manufacturer but disseminated by the local authority.

The information must be publicly available but is specifically disseminated to those liable to be affected by the hazard, as determined by the HSE. The distance selected by the HSE often corresponds to the consultation distance. The actual information to be provided is given in Schedule 8 of the regulations, and may be summarized as: an explanation of the activity undertaken at the site; the names of the substances involved and a description of their hazards; general information about the nature of major accidents, including their potential effects on the surrounding population and environment; and information on how the population will be warned and kept informed and on what action they should take in the event of an accident.

24.17.1 Information booklets

Information may be issued in the form of an information booklet for householders. An example is *Canvey Island: Advice to Householders* (Essex County Council, n.d.). This has sections dealing with: warnings; flooding; large-scale fire, explosion, shipping, aircraft, road transport emergency or escaped gases; evacuation and emergency routes; rest centres and emergency feeding; a special register of the infirm and incapacitated; medical and first aid; restoration and rehousing; people at work; pets and livestock; allocated accommodation; police sectors; and enquiries and information. The booklet also contains a map of emergency routes and an emergency procedure checklist.

24.18 Safety Case Guidance

Emergency planning for major hazard installations is intimately bound up with the safety case for such installations. The safety case develops the scenarios on which emergency planning is based both in respect of the initial release and of subsequent escalation and mitigation.

Guidance on safety cases is available for a number of chemicals found in major hazard installations. Guides include *A Guide to the Writing of LPG Safety Reports* by the Liquefied Petroleum Gas Industry Technical Association (LPGITA) (1988), *General Guidance on Emergency Planning within the CIMAH Regulations for Chlorine Installations* by the Chlorine Sector Group of the CIA (1987, 1989), *The CIMAH Safety Case: Ammonia* (CIA, 1988/PA9), *A Method for Estimating the Offsite Risks from Bulk Storage of Liquefied Oxygen (LOX)* by the British Compressed Gases Association (BCGA) (1984) and *Guidance Note. Safety Case for Ammonium Nitrate Required by Regulation 7 of CIMAH* by the Fertilizer Manufacturers Association (FMA) (1989).

Further guidance has been provided by Cassidy and Pantony (1988), who give a number of tables listing for fire, explosion and toxic release sets of events of decreasing frequency but increasing severity together with the range to defined levels of harm. Several of these tables are given in Chapter 9.

24.19 Evacuation and Shelter

Fire and explosion events tend to occur over such a short time scale that evacuation is not practical. The principal event where evacuation may be in question is a large release of toxic gas. In this case an alternative means of mitigation is shelter within buildings, so that the question becomes a choice of evacuation vs shelter. This question is discussed by Lynskey (1985), Purdy and Davies (1985; 1985 LPB 65) and Essery (1991).

Considering first shelter, a model for the toxic gas concentrations outdoors and indoors during the passage of a toxic gas cloud, and for the associated toxic loads, has been given by Purdy and Davies (1985). A building with a ventilation rate of 2 air changes/hour offers a degree of protection which reduces the toxic load for a person indoors compared with that for someone outdoors by at least an order of magnitude, although protection is much reduced if the ventilation rates are higher. A high degree of protection can therefore be achieved by advising people to stay indoors and shut doors and windows. A further reduction in the overall toxic load can be obtained if at the appropriate time persons indoors leave the still contaminated indoor space and come outdoors into the fresh air.

The authors argue in effect that the degree of protection provided by shelter is such that it should be policy for a toxic gas release to use shelter rather than evacuation, except in certain special circumstances.

The choice between shelter and evacuation is also considered by Essery (1991), who discusses the Nanticoke incident in 1987 in which some people remained in shelter and some were evacuated (Duclos, Binder and Rieter, 1989). Although not statistically significant, of the nine interviewees who chose not to evacuate, only one may have been affected, whilst of the 1275 who did evacuate some 20% were affected. He states also that for chlorine with a probit equation of the usual form ($n = 2.75$), for a release lasting 20 minutes and with a building with 2 air changes/hour, the fraction of the lethal toxic load received by someone inside would be only 4% for the case where someone outside received 100% of that load.

As regards evacuation, the following three cases may be distinguished: (1) evacuation after a toxic release has taken place, (2) evacuation when a toxic release is expected, and (3) evacuation after the toxic gas cloud has passed.

Taking these cases in turn, it needs to be appreciated that once a toxic leak has occurred, the cloud may travel quite rapidly. Even at a low wind speed of 2 m/s the cloud will travel 1.2 km in 10 minutes, whilst at the higher wind speed of 5 m/s it will travel 3 km.

The event in which evacuation is most likely to be considered is where a tank or vessel is under threat, usually from fire, and there may well be a loss of containment, but only after some time has elapsed. This is the situation for which evacuation is most often considered to be an option. Even here, there are a number of difficulties.

Data from incidents in the UK indicate that the decision to evacuate is unlikely to be made within the first half hour. In the Mississauga incident, described below, this decision came only after 3 hours had elapsed. Purdy and Davies state that the assumption made in one of the more sophisticated emergency plans for a large chemical site in the UK is that it would take 40 minutes after the start of an incident before a police car arrives in a nearby housing estate.

Even when the decision has been taken, its implementation by the police is not straightforward. Unlike the fire brigade, the police are not normally equipped with respiratory protection.

It cannot be assumed that people at risk will necessarily heed the advice to evacuate. The study by Hans and Sell (1974), quoted in Chapter 9, found that although the behaviour of the public was rational rather than panicky, there was a problem in getting people to move.

Purdy and Davies suggest that there may be scope for post-incident measures, to reduce the toxic load for persons indoors where the space is still contaminated by advising them to come outdoors when the gas concentration is lower, and possibly evacuating them.

In these circumstances there is likely to be a proportion of the population who will be suffering from the gas and who will therefore need assistance.

In short, although the off-site emergency plan will normally include an evacuation plan, it is likely to recognize that shelter rather than evacuation is the preferred option.

Models for evacuation have been discussed in Chapter 9 and those for shelter in Chapter 15.

24.20 Transport Emergency Planning

As described in Chapter 23, it is essential for hazardous chemicals to be transported in tanks and containers designed and maintained to high standards, for transport personnel to have any necessary training, for comparative studies of the different means of transport to be done and routes carefully selected, and for hazard studies to be carried out. Even so, it is still necessary to plan for possible transport emergencies.

As with safety in the transport of hazardous chemicals in general, so with transport emergency planning the chemical industry has always tended to take the view that although strictly the responsibility lies with the shipper, it is very much in the interests and responsibility of the industry also to take measures to deal with transport emergencies. This attitude finds practical expression in companies' willingness to send emergency teams to situations in which their own products are not involved.

Transport emergency planning has something in common with works emergency planning, but there are some important differences. The main one is that even with careful routing there is a vast range of locations at which the emergency can occur.

The elements of transport emergency planning include: (1) chemical data; (2) information and labelling; (3) incident control network; (4) emergency procedures; (5) emergency teams; (6) outside services; and (7) public relations. These elements are now considered in turn.

24.20.1 Chemical data

Although the properties of chemicals that are shipped are usually well enough understood for most purposes, it is necessary for particular attention to be paid to any properties which may be specially important in a transport emergency.

In the Glendora incident described below, 30 000 people were evacuated because it was feared that lethal quantities of phosgene might be generated by burning vinyl chloride monomer. Although the manufacturer's expert on the spot discounted this hazard, the authorities proceeded with the evacuation. The incident led the industry to carry out research to determine more exactly the extent of the hazard from this source, which turned out to be small.

24.20.2 Information and labelling

People involved in a transport incident need information about the chemical, but their needs differ. The amount of information required is different for the public, the personnel involved in the first few minutes and for those involved in longer term incident control and clearing up operations.

There are also different sources of information. The most accessible is the labelling of the container with a placard. Then there is usually more detailed information carried somewhere on the vehicle. The shipper and outside services, such as police and fire services, should have manuals which give similar data. Finally, there is the manufacturer who may be contacted through the national incident control network.

A review of the principles of labelling systems is given in *An Assessment of Precautionary Labelling Systems Relating to the Movement of Petroleum Products in Bulk* (CONCAWE, 1977 7/77). The elements of such a labelling system are (1) product identification, (2) an action code, (3) a property code and (4) a hazard symbol.

The product identification should follow a recognized classification. There is a United Nations (UN) classification, and other classifications are those of the *European Agreement Concerning the International Carriage of Dangerous Goods by Road* (ADR) and the *International Regulations Concerning the Carriage of Dangerous Goods by Rail* (RID).

The action code should give immediate information on the action to be taken, should indicate the hazards to which the emergency service personnel and the public could be exposed, and should be simple to understand.

The property code should indicate the hazardous properties of the chemical and/or the degree of hazard.

In the UK, the HAZCHEM scheme, which is described in *Hazard Identification – A Voluntary Scheme for the Marking of Tank Vehicles and Dangerous Substances* (CIA, 1975), constitutes such a labelling system.

The hazard warning signs and hazard symbols used in the UK are shown in Plates 21 and 22, respectively. The hazard symbols are official government symbols and are given in the Highway Code (DoT, 1978). They are used in the HAZCHEM scheme.

Plate 23 shows the HAZCHEM guide and Plate 24 the HAZCHEM sign. The panel shows the HAZCHEM code number (2PE), the UN classification number (1230), the telephone number to ring in case of an emergency, and the hazard symbol.

The HAZCHEM code gives information under the following headings: (1) fire fighting number, (2) personal protection, (3) risk of violent reactions, (4) spillage action and (5) evacuation.

The HAZCHEM code number consists of one figure and one or two letters, e.g. 2PE. The figures 1, 2, 3, 4 refer to the fire fighting methods to be used. The first letter P, R, S, T, or W, X, Y, Z refers to the spillage action to be taken. The second letter E is added where there is a need to consider evacuation of the area.

There is, in addition, the TREMCARDS system (CIA/2). A typical TREMCARD is shown in Plate 25. These are cards carried with the vehicle which give more detailed information and instructions.

24.20.3 Emergency procedures

There are certain priority actions which should be taken by the person at the scene of the incident. These are to: (1) keep people away; (2) inform incident control; (3) contain the chemical; (4) avoid igniting the chemical; and (5) obtain chemical data.

The communication with the incident control centre is important. The centre should be informed of: (1) the

place and time of the incident; (2) the chemical involved; (3) the condition of the container; (4) any injuries or deaths; (5) the surrounding area (open country, town); (6) the weather conditions; (7) the assistance available (police, fire services); and (8) the means of maintaining contact.

It is particularly important for the man on the spot to ensure that the control centre can keep in contact with him, by giving a telephone number or otherwise. Communications may be greatly assisted by the use of mobile telephones.

The chemical should be kept in a container as far as possible. If there is a leak, any liquid should be contained by an improvised bund. The chemical should not be allowed to get into sewers. A pool of liquid may often be rendered more safe by covering it with a blanket of suitable foam.

Ignition of the material should be avoided if at all possible. Sources of ignition should be kept well away.

Some chemicals that are transported have properties which may increase the hazard of the incident. These include (1) a low boiling point, (2) a capacity for spontaneous ignition and (3) reaction with water.

24.20.4 Emergency teams

The manufacturer of a hazardous chemical normally arranges for an emergency team to be available to be sent to the scene as soon as a transport emergency is notified. In some cases this involves mutual assistance schemes.

The personnel comprising the emergency team are usually thoroughly familiar with the chemical and are trained in handling incidents.

In addition to the general incident control measures already described, the emergency team usually has expertize in dealing with leaks and fires and in emptying damaged containers and clearing up.

A moderate leak may often be plugged with wood or special materials.

A leak or spillage should not be ignited. If a leak has ignited, however, it may be the best policy to let it continue burning. The danger of putting out a fire without eliminating the leak is that the amount of flammables may build up and, if re-ignited, cause a more serious fire or explosion.

If other containers are present, as it typically the case in rail incidents, it may be necessary to cool these with water to prevent their overheating.

The equipment carried by an emergency team varies according to the chemical involved, but may include items such as (1) chemical data, (2) protective clothing, (3) breathing apparatus, (4) a safety harness and line, (5) general tools and flashlights, (6) leak plugging equipment (e.g. wood plugs), (7) analytical equipment (e.g. explosimeter), (8) floodlights with generators and (9) a first aid kit.

The emergency team is sent as soon as possible on receipt of notification, but several hours are likely to elapse before it reaches the scene of the incident.

24.20.5 External services

The general role of the external services such as the police and fire services has already been described. Some additional points relevant to transport emergencies may be mentioned briefly.

A transport emergency differs from a works emergency in that it does not occur on a fixed site. There is therefore much less scope for advance co-operation between a manufacturer and the services in his local authority area. The variety of hazardous chemicals which the services may have to handle is much greater.

It is therefore essential for there to be close co-operation at the national level between the industry and these services. In particular, full information should be provided about the chemicals. In the UK, the measures described, such as the TREMCARD system and the National Chemical Emergency Centre, provide such information.

Although information cards may be carried on the vehicle, it should be borne in mind that in some cases these may not be accessible.

Another feature of a transport emergency is that it may well occur in a built-up area. This means that measures to keep people away from the scene, to divert traffic, to maintain access for emergency vehicles and possibly to evacuate the population assume particular importance.

Decisions on the advice to be given to the public, whether this be to take shelter or to evacuate, are particularly difficult, as the Glendora and Mississauga incidents show. In some situations where it is not strictly necessary to involve large numbers of people, the authorities may nevertheless have little choice but to order action, unless precise information is available to them on the hazards of the chemical, particularly the toxic hazards.

Likewise, information on fighting fires of the chemical is important for the fire services. In particular, the latter need to know whether the chemical reacts violently with water.

24.20.6 Public relations

The conduct of public relations for works emergencies has been considered above. There are several points which are particularly relevant to transport emergencies. As always, there should be no attempt to cover up either the known hazards of the chemical or the actual incident which has occurred.

In a transport emergency there is not just one party, but two (the carrier and the shipper) who are perceived as responsible by press and public. Co-ordination both before and during the event between the manufacturer and the carrier on public relations aspects is therefore in order.

Personnel who may be involved in an incident, such as the driver and the emergency team, need to be briefed on dealing with the press. Unnecessary speculation about the cause of the incident or comment about the end uses of the chemical should be avoided.

24.20.7 Minor incidents

It should not be assumed that all incidents arising from the transport of chemicals are necessarily emergencies. The majority are in fact quite minor incidents, not involving any kind of crash and comprising only small leaks or even merely odours.

24.20.8 Rail transport

The foregoing account has been concerned primarily with road transport, but most of it is applicable to rail

transport also. In this case the railway authority establishes its own procedures and trains its own personnel. Again the prime requirement from the manufacturer is full information about the chemicals.

Emergencies involving hazardous chemicals on railways tend to have some special features. One is the problem of access, particularly for fire engines. The track is often blocked by derailed rail vehicles. Another aspect is that there are usually a number of tank cars involved, with the danger of a spread of the fire/explosion. Frequently there is a hazard to other transport, such as to trains on other tracks, or to nearby roads.

24.21 Transport Emergency Arrangements

24.21.1 CHEMSAFE

In the UK there exists an incident control network in the form of the Chemical Industry Scheme for Assistance in Freight Emergencies (CHEMSAFE), which came into existence 1974. This evolved from the G Centres set up by ICI in the mid-1960s to provide information and emergency teams for transport incidents (Walmsley, 1973). The scheme is described in the *CHEMSAFE Manual* (CIA, 1991/RC32). The scheme has developed over the years. Many of the original elements have been subsumed in regulations. The scheme itself, which applied originally to road transport, has been extended to cover rail, sea and air.

The purpose of the scheme is to create a network of companies committed to providing assistance in the event of a transport incident. There are three levels of participation in the scheme and participants commit themselves to provide: A, information; B, help at the scene, for their own products; and C, help at the scene, for any products.

The *CHEMSAFE Manual* provides advice to participating companies on setting up a procedure for participation, training of personnel for their different roles, and legal liability and insurance.

24.21.2 National Chemical Emergency Centre

As a back-up to the CHEMSAFE scheme, the National Chemical Emergency Centre (NCEC) at Harwell provides a round-the-clock information point for public emergency services. It is an alternative source of information when a manufacturer cannot readily be contacted.

The NCEC is able to furnish information on the hazards of chemicals transported, on the assistance available in the event of an incident and on methods of dealing with spills and fires, and can put the emergency services in contact with a CHEMSAFE level C company.

24.21.3 Mutual aid arrangements

The CHEMSAFE scheme is complemented by mutual aid arrangements, which are of two types. One is the inter-company arrangement in which companies agree to assist each other, thus ensuring a wider geographical coverage and a more rapid response. The other is the local arrangement involving several companies in one locality, developed to avoid unnecessary duplication of emergency centres or to give coverage of specific local areas.

One such scheme is that for chlorine, which is described in *Inter-company Collaboration for Chlorine Emergencies* (CIA, 1983, 1992 RC48). The guide describes the scheme, lists the participating companies and give the procedures to be followed in an emergency, starting with the notification to the manufacturer and ending with media relationships and restoration after the incident; it does not cover technical aspects such as spill control or fire fighting.

There is a similar scheme for ammonia, described in *Inter-company Collaboration for Ammonia Transport Emergencies* (CIA, 1982).

24.21.4 US system

There is an essentially similar system for transport emergencies in the USA, organized by the CMA. An account is given by Resen (1986).

The basis is the Chemical Transportation Emergency Center (CHEMTREC), created in 1971. Its origins are described by Bigelow (1970, 1971). As in the UK, chlorine was the subject of one early scheme, the Chlorine Out-Plant Emergency Plan (COPEP), operated by the Chlorine Institute (R.L. Mitchell, 1971). CHEMTREC acts as a communications centre for shippers, carriers and mutual aid groups, which operates round the clock. It can provide information on chemicals and can contact a shipper for more information or assistance.

CHEMTREC is complemented by CHEMNET, a mutual aid arrangement.

The CMA operates a comprehensive system of training for transport emergencies, covering case histories and topics such as patching and handling leaks, transfer from tank trucks and tank cars, and clean-up techniques.

24.22 Spectators

An incident which lasts for any appreciable length of time is liable to attract spectators. This is true not only of transport incidents occurring outside the site, but also of incidents on site which are visible outside.

The effect of spectators is two-fold. The number of people at risk may be considerably increased, and the passages for the emergency services can become congested, with consequent delays.

The problem of spectators has been investigated by Hymes (1985 LPB 65), who describes a quite large number of incidents in which spectators suffered injury. Some of the cases cited involve people who became exposed to the threat and stood watching it develop instead of making their escape, whilst in others they were attracted to the incident as sightseers. Some of the incidents which he describes are summarized in Section 24.23.

The control of spectators is therefore an essential part of an off-site emergency plan and of a transport emergency plan. The responsibility for such control rests with the police.

24.23 Emergency Incidents

24.23.1 Historical data

Some information on emergencies in the process industries has been obtained in the course of a study on human factors as a cause of pipework failures by Bellamy, Geyer and Astley (1989).

For failures of mitigation the number of incidents due to each cause were as follows: delay, 23 (45%); design deficiency, 14 (27.5%); and lack of resources, 14 (27.5%). Examples in the first category were lack of procedures for handling the incident and defective fire fighting equipment; in the second category examples were a layout leaving insufficient space for fire water jets to be directed at the source of the fire and the inaccessibility of shut-down equipment due to the leak itself; and in the third category, examples were a lack of manpower and a lack of equipment.

The information on the implementation of emergency plans and on evacuation in this study is ambiguous. On the one hand, there were 42 cases recorded in which an emergency plan was put into effect. In 27 of these cases the plan implemented was the on-site plan and in 11 it was the off-site plan; in the 4 remaining cases the plan was not specified. On the other hand, there were 30 cases in which there was evacuation, either on-site or off-site or both, with 13 on-site and 24 off-site evacuations.

24.23.2 Incidents involving evacuation and/or shelter

There have been a number of instructive incidents involving evacuation and/or shelter. They include those at La Barre in 1961, Glendora in 1969, Potchefstroom in 1973, Houston in 1976, and Mississauga in 1979.

In 1961 a rail crash occurred at La Barre, Louisiana, involving a chlorine rail tank car, only 50 yd from a house (Case History A29). A father was looking after a baby in the house, the infant began to choke and gasp, and the frantic father carried it outside, where the gas concentration was higher still. The child died in hospital.

In 1969 a group of eight rail tank cars containing vinyl chloride monomer (VCM) were involved in a crash at Glendora, Mississippi, and one started to leak (Case History A43). That evening one of the tank cars ruptured, with subsequent ignition of the leak. A heavy fog was observed over the area and it was considered that it might be VCM. Those dealing with the incident consulted the *Handbook of Hazardous Materials*, which stated that in a VCM fire phosgene could be formed. Further advice was sought from the manufacturer's representative, who stated that the principal problem was likely to be HCl and smoke, and university chemists, who stated that burning VCM could create phosgene which was potentially dangerous up to a radius of 35 miles. An evacuation was initiated involving some 30 000 people.

In 1973 a sudden failure occurred in an anhydrous ammonia storage tank at Potchefstroom in South Africa (Case History A65). Workers in a building 80 m from the release survived, but people who left their houses 180–200 m from it died.

In 1976 at Houston, Texas, a tank truck carrying 19 ton of anhydrous ammonia ruptured at a highway intersection (Case History A84). The resultant gas cloud enveloped the Houston Post building but the workers inside were not affected. Outside 94 people caught in the cloud were injured, of whom 5 died.

The implications of such incidents for evacuation and shelter have been discussed by Purdy and Davies (1985, 1985 LPB 62).

24.23.3 Mississauga

A very large evacuation occurred on Saturday 10 November 1979 at Mississauga, near Toronto (Case History A97). At 23.52 that night a train crash occurred which resulted in fires and explosions involving several propane rail tank cars. The train manifest was found, but it was in code. A strong smell of chlorine was detected. At 01.30 the next morning a readable version of the manifest was obtained. A rail tank car containing some 90 te of chlorine was identified as being in the train and it was concluded that this car was amongst the burning wreckage. At 03.00 the decision was taken to evacuate the surrounding population. An evacuation was begun which involved a total of about 215 000 people. The chlorine tank car was identified by helicopter and found to have a visible hole in it. At 09.00 on Tuesday morning an initial attempt was made to plug the hole, but this failed; a second attempt later was successful. The tank was subsequently emptied, some 18 te of chlorine being eventually removed. During Tuesday afternoon 143 000 evacuees were allowed to return to their homes in the areas more distant from the crash. The rest returned only after a total absence of 6 days.

24.23.4 Incidents involving spectators

The following incidents have been described in the study of spectators already mentioned by Hymes (1985 LPB 65).

At Deer Lake, Pennsylvania, in 1959, a road tanker carrying LPG was struck by a following truck in a wet street (Case History A27). LPG was released and ignited, engulfing the rear of the tanker. Fire services arrived, but expended water on a nearby building, and in due course the tanker suffered a boiling liquid expanding vapour explosion (BLEVE). Fragments, which included most of the tank, killed 11 spectators and injured 10 more. Emergency services were hampered both before the rupture and after it.

At Meldrin, Georgia, in 1959, a rail tank car suffered a partial rupture near a picnic site. A large gas cloud spread and for some time did not ignite (Case History A28). When it did ignite a flash fire occurred. There were 23 dead, many of whom were found in their cars. Emergency services were greatly hampered because the site was remote and served only by a dirt road congested by spectators and relatives of the casualties.

At Kingman, Arizona, in 1973, a jumbo rail tank car carrying propane developed a leak which ignited (Case History A63). Despite police discouragement a large crowd of spectators jostled to get a view. In due course the tank car underwent a BLEVE and a huge fireball erupted. Some 90 spectators 300 m away suffered injury.

At San Carlos de la Rapita, Spain, in 1978, a road tanker carrying propylene past the Los Alfaques campsite ruptured with a small explosion. A flammable gas cloud began to spread through the site. Campers who did not appreciate that the full hazard from the burning tanker had yet to develop stood around bemused whilst escape was still possible. Many wore bathing suits or light beachwear. There followed a major explosion and flash fire. The eventual death toll was about 210, a large proportion from severe burns. This incident is described further in Appendix 16.

Other incidents in which many of the deaths occurred among spectators are those at Texas City in 1947 (Case

History A16), and Caracas, Venezuela, in 1982 (Case History A102). In the Texas City disaster a fire developed aboard a ship, the *Grandcamp*, in the harbour. The ship was carrying ammonium nitrate. In due course the ship disintegrated in an enormous explosion, killing all those in the dock, including firemen and spectators. This explosion and a further one in another ammonium nitrate carrier, the *High Flyer*, killed 552 people and injured another 3000.

The Caracas disaster involved a fire in a oil tank sited on a hill. A boilover occurred and the burning oil flowed down the hill. Forty firemen were killed, together with many civil defence workers and spectators, giving a death toll of 153 with 7 missing.

24.24 Emergency Aftermath

Most accounts of emergency planning concentrate not unnaturally on the prior planning for the emergency and the emergency itself. Some thought should be given, however, to the aftermath.

24.24.1 Contaminated land

One physical consequence of an incident may be contaminated land. The decontamination of land is a specialist topic. Guidance is given in *Reclamation of Contaminated Land* by the Society of Chemical Industry (SCI) (1980) and *Remedial Processes for Contaminated Land* (Pratt, 1993). This topic is also treated in Appendix 11.

24.24.2 Survivors

The survivors of a large multiple fatality accident suffer the effects long afterwards. Some effects are physical injury and physical and mental illness, including stress, and feelings of guilt.

A disorder characteristic of major accidents is post-traumatic stress disorder (PTSD). A study of this effect following an accident at a factory in Norway in 1976 has been described by Weisaeth (1988, 1992). A leak of flammable fluid occurred within a building, a flammable mixture formed through large parts of the building and found a source of ignition, and the resultant explosion demolished the whole building, killing six people. A study was made of the condition of the survivors, particularly that of the most severely affected group of 66 people. In this group 37% demonstrated optimal disaster behaviour and 43% developed PTSD. The proportion exhibiting the disorder fell to 37% at 7 months and 19% at 3 years after the accident. Conclusions were that if the illness was still severe after 7 months it was liable to become chronic, that there was a marked improvement in the more moderate cases between 7 months and 3 years, and that in hardly any of the cases did the reactions disappear completely within the 3 years. It should be mentioned that by the second day after the accident all employees were given a guarantee of continued employment, thus removing one potential cause of additional stress.

24.24.3 Community

A large multiple fatality accident has a significant and long-lasting impact on the local community. This impact can be expected to be particularly severe if that community is a relatively small and closed one, such as a fishing or mining village.

That the community's response is conditioned by the local culture is shown by a study of the impact of the Friuli earthquake of 1976 by Geipel (1982, 1991). A comparison of the response of the local community there to that of another community in Southern Italy to an earthquake in 1980 revealed a marked difference. At Friuli, solidarity between victims and helpers was soon established, whereas the southern community was distrustful of both state and international aid – 'What good will come out of Rome?'

25 Personal Safety

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The majority of injuries or deaths on process plants are the result not of high technology but of quite simple situations. The number of people involved in a single accident is usually only one or two. Thus, although loss prevention is particularly concerned with technical aspects, it is appropriate nevertheless to devote some consideration to hazards to the person and to their control.

Moreover, the loss prevention approach has a contribution to make in this area also. The same management discipline is required to deliver good performance in the personal safety area as in that of high technology. Three aspects appear particularly relevant: formal systems and procedures, hazard identification and hazard assessment.

In addition to injuries from accidents workers may also suffer impairment of health which sometimes becomes apparent only over a long period. It is necessary, therefore, to make some mention of this type of hazard and its control by occupational health measures.

Personal safety is dealt with in a large number of texts, which include *Safety and Management* by the Association of British Chemical Manufacturers (ABCM) (1964/3), *Industrial Safety Handbook* (Handley, 1969, 1977), *Industrial Hazard and Safety Handbook* (R. King and Magid, 1979), *Safety and Accident Prevention in Chemical Operations* (H.H. Fawcett and Wood, 1982), and *Safety at Work* (Ridley, 1993–) and *Safety in the Process Industries* (R. King, 1990). Selected references on personal health and safety are given in Table 25.1.

Table 25.1 *Selected references on personal health and safety*

API (EA-7402); FPA (S9, S10); HM Chief Inspector of Factories (annual); National Institute of Industrial Psychology (n.d.); OSHA (n.d./3, OSHA 2237, 1990/6); RoSPA (IS/106); MCA (1962–/1–4); M.E. Webb (1962); D.B. Campbell (1965); Berry (1969, 1977); Kershaw (1969); ILO (1972, 1980b); Robens (1972); McCormick (1974); Bond and Bryans (1975); PITB (1975 Safety Training Guide 1); Kershaw and Symons (1977); Atherley (1978); R. King and Magid (1979); Bulloff (1987); H.E. Nelson (1987); NFPA (1991 NFPA 101, 1992 NFPA 101M, 1994/40)

Human factors (see also Tables 14.1, 14.2 and 14.11)
Hands (1969); AIHA (1971/1); Singleton (1976b); Stoecker (1976); Atherley (1977b); Dumitriu (1977); Hale and Glendon (1987); HSE (1989 HS(G) 48); ACGIH (1992/76)

Occupational hygiene, industrial hygiene
ACGIH (Appendix 28); ASTM (STP 164); Gauvain (n.d.); HSE (Appendix 28 *Medical*, *SHW Leaflets*, SIR 8, 1977e, 1982 HS(G) 20, 1984 SHW 395, 1987 *Oil Industry* 2, 1993 CRR 57); MCA (SG-1); NIOSH (n.d./3, 1974 Crit. Doc. 75–126, 1977/4, 1979/5, 1980/22, 1981/6, 1985/8, 1988/9, 24, 1987/11, 1989/25, 1990/19, 1991/20, 1992/21); NSC (n.d./3, 1988/9, 1989/10); Harvey and Murray (1958); Hunter (1959, 1975); R.T. Johnson and Miller (1960); W.H. Meyer and Church (1961); Ministry of Labour (1962); Mort (1965); Coates (1966); SCI (1968); M.H. Hall (1969); Mayers (1969); Wilcox (1970); McElroy and Olishifski (1971); Schilling (1973); Kusnetz (1974); J.F. Morgan (1974); Socha (1974); AIHA (1975/2, 1984/7, 1988/14, 15, 1990/19); Scherberger (1977); Vlad (1977); Anon. (1978e); Atherley (1978); Munn (1978); D. Turner (1978); R. King and Magid (1979); Kohn (1979a); Thiess and Zapp (1979); Waldron (1979, 1989); Harvey (1980–); P. Lewis (1980); Waldron and Harrington (1980); Widmer (1980); Burgess (1981); Chissick and Derricott (1981); Cullis and Firth (1981); Woolhead (1981); D. Farmer (1982); Gill and Ashton (1982); Selman (1982); Harrington and Gill (1983–); Murphy (1982); T.J. Rose and Nourish (1982); BOHS (1983 Monogr. 10); Constance (1983); First (1983); IBC (1982/27, 30); ILO (1983/1); Kusnetz and Phillips (1983); Parmeggiani (1983); ASME (1984/196); CIA (1984 RC13); CONCAWE (1984 84/54, 1986 86/69, 1987 87/57); Wang (1984); J.R.P. Clarke (1985); HSC (1986/6); Cralley and Cralley (1987); Foa *et al.* (1987); Lipton and Lynch (1987, 1994); Ricci and Cox (1987); Noma *et al.* (1988); R.M. Scott (1989); Abdullah and Yacob (1990); API (1990 Publ. 4519); Burge (1990); Carson and Mumford (1990 LPB 91); Dees and Taylor (1990); J.C. Edwards and Bujac (1990); Phoon and Tan (1990); Wolff (1990); Ryder (1991); IP (1993 MCSP Pt 18, 1993/3); Lin *et al.* (1993); Phoon (1993)
Skin diseases, dermatitis: BSC (n.d./3, 9); Department of Health Education and Welfare (n.d.); HSE (HSW Bklt 18, 1974 MS(B) 1, 1975 SHW 367, 1982 SHW 397, 1981 EH 26, 1983 MS(B) 6, 1990 EH 58, 1991 MS 24); R.P. White (1934); L. Schwartz, Tulipan and Birmingham (1957); McCreanney (1969, 1977); Fregert (1974); Levene and Calnan (1974); Rycroft (1979, 1980, 1980 LPB 33); McNaughton (1982); Gadian (1983); W.A.D. Griffiths and Wilkinson (1985)
Allergies, asthma: Eppe, Fontanges and Grollier-Baron (1980); BOHS (1984 Monogr. 12); HSE (1991 MS 25)

Workplace exposure, environmental control, exposure monitoring
ACGIH (Appendix 28); AIHA (Appendix 28); ASTM (STP 164); HSE (MS 18, 1989 EH 42, 1990 HS(G) 61, 1992 EH 56); MCA (1968/15); Linch (1974, 1981); Newcombe (1974); API (1975 Publ. 4262); Chemical Society (1975); Zatek (1975); Marion (1979); Jardas (1980); Kung (1980); IBC (1981/14); British Gas (1987 TIN 25); Thorsen and Mølhave (1987); Grumbles (1990)

Analysis of working atmosphere, analytical methods
DoEm (Det. Bklts series); HSE (MSDS series); Sunshine (1969); ACGIH (1972, 1988/24, 1989/27); Associated Octel Co. (1974 Bull. 18); Lisk (1974); CIA (1975/8); Ratcliff (1975); Thain (1976); NIOSH (1977–78/2, 1978/1); Groves (1978); G.L. Lee (1980); Walton (1980); ASTM (1981 STP 721, 1982 STP 786); Lauwerys (1983); Lloyd (1987); OSHA (1990/5); AIHA (1993/9, 27)
BS (Appendix 27 *Analytical Methods*)

COSHH, including assessments
CIA (1989 RC9, RC11, 1990 RC10, RC12, 1991 RC38, RC39); HSE (1989/24, IND(G) 64(L), 65(L), 67(L), 1990/28); Hewitt (1991); Hopkin (1991); Luxon (1991); Samuels (1991)

Severe physical conditions
C.N. Davies, Davis and Tyrer (1967); Harrington (1980b); NIOSH (1987/15)
Hot environments: NIOSH (1972 Crit. Doc. 72–10269; 1986 Crit. Doc. 86–113); Bedford (1974); Gill (1980a); ASHRAE (1985 ASHRAE 55); Jefri and Daous (1989); McGrath (1993)
Environmental control: Bedford (1974); Waldron (1980b)

Corrosive chemicals
MCA (SG-1); OSHA (OSHA 2237); Harford (1969); W.I. Morton (1976); E.L. M. Roberts (1977); HSE (1984 SHW 395)

Dust, including asbestos (see Table 18.1)

Aerosols (see Table 18.1)

Ventilation
HSE (SIR 16, 1975a, 1975 TDN 19, 1987 HS(G) 37, 1988 EH 22, 1990 HS(G) 54); Walls and Metzner (1962); Hemeon (1963); ACGIH (1968, 1982/6, 1988/21, 1989/38, 1991/58, 66–69); Grandidge (1969); IHVE (1970); ASHRAE (1972, 1973, 1988 ASHRAE 11, 1989 ASHRAE 62, 1991/4, 5, 1992/6, 1993/7); Baturin (1972); Leach and Bloomfield (1973, 1974 BRE CP 36/74); Mecklenburgh (1973, 1976, 1985); Bedford (1974); Croome-Gale and Roberts (1975); MacDermott (1976); Anon. (1977 LPB 15, p. 10); CIBS (1977a,b); CIBSE (1977, 1978–); Gill (1980b); ASTM (1982 STP 719); Caplan (1982); Goodfellow and Smith (1982); Anon. (1983 LPB 49, p. 15); Walsh, Dudney and Copenhauer (1983); Mitler (1984); Constance (1985); Goodfellow (1985, 1986); Hayashi *et al.* (1985); Huebener and Hughes (1985); M.R. Marshall (1983); Cassells (1986–); Fanger and Christensen (1986); M.R. Marshall and Stewart Darling (1986); BOHS (1987); Anon. (1988 LPB 80, p. 20); AIHA (1991/21, 22, 1993/25); Eycott (1989); J.C. Edwards and Bujac (1990); Andreopoulos, Karayanis and Markatos (1992); NFPA (1992 NFPA 91, 1993 NFPA 90A); McGrath (1993); ANSI Z9 series, ANSI Z9.2–1979, ANSI Z9.1–1991; BS 5720: 1979, BS 5925: 1991
Local exhaust ventilation: Dallavalle (1952); B. Fletcher (1977); Bender (1979); Goldfield (1980); Goodfellow and Bender (1980); D. Hughes (1980); Piney and Carrol (1983); J.D. Cook and Hughes (1986); B. Fletcher and Johnson (1986); Saunders (1987)

Compressed air
American Oil Co. (n.d./2); BSC (n.d./1); Paterson (1969, 1977); HSE (1989f, 1990 HS(G) 39)

Inert gas
Kletz (1980f); Anon. (1991 LPB 97, p. 5); Anon. (1991 LPB 102, p. 25); Anon. (1993 LPB 110, p. 8); Anon. (1993 LPB 112, p. 20)

Electricity
American Oil Co (n.d./5); HSE (HSW Bklt 31, 1984 GS 27, 1985 GS 37, 1986 GS 38); RoSPA (IS/73); Haigh (1969); Consumers Association (1972); Bland (1977); Crom (1977); Eales (1977a,b); W.R. Lee (1977); BOHS (1985 Monogr. 2); Fordham Cooper (1986); Anon. (1990 LPB 92, p. 22); Anon. (1991 LPB 102, p. 25); Marks (1991); NFPA (1993 NFC 70); Anon. (1994 LPB 118, p. 16)
BS (Appendix 27 *Electrical*)

Non-ionizing radiations
ACGIH (n.d./12, 1990/48); WHO (EHC 14); Battocletti (1976); AIHA (1977–/3); BOHS (1978 Monogr. 1); Harrington (1980b); Kanagasabay (1980); Chowdhury (1982); Kielman and Fawcett (1982); McKinlay (1982)

Ionizing radiations (see also Table A20.1)
ACGIH (n.d./12, 1990/48); MRC (1956, 1975a); Wiltshire (1957); Imperial College (1958); Blatz (1959); Cherubin (1960); US Congress, Joint Committee on Atomic Energy (1960); Kuhn (1964); H.H. Fawcett (1965c); CVCP (1966); P.S. Baker (1968); Black and Horn (1968); Coombe (1968); Department of Employment and Productivity (1968); Bennellick (1969); HSE (1970 HSW Bklt 13); L.S. Taylor (1971); NAS/NRC (1972c); Shapiro (1972); ICRP (1977c, 1979); Brodsky (1978–); R. King and Magid (1979); Doran (1980); Harrington (1980b); Holiday (1980 LPB 35); Dennis (1982); Kielman and Fawcett (1982); UN Scientific Committee on Effects of Atomic Radiation (1977, 1982); BOHS (1982 Monogr. 5); Chilton, Shultis and Faw (1984); NFPA (1991 NFPA 801)
BS (Appendix 27 *Radioactivity*)

Lasers
ACGIH (n.d., 1990/41); Sliney and Wolbarsht (1980); Weber (1982); Winburn (1987, 1990); Pilborough (1989); CVCP (1992)
BS 7192: 1989, BS EN 60825: 1992

Physical chemistry
Leach (1967); Jennings (1974a,b); Keey (1977)

Lifting and carrying
HSE (HSW Bklt 1, 1971 HSW Bklt 47, 1978 PM 16, 1981 PM 21, 27, 1985 PM 54, *Research Review* 2, 1986 GS 39, 1993 PM 15); Halliday (1969); R. King and Magid (1979); Ayoub, Mital, Asfur *et al.* (1980); Ayoub, Mital, Bakeen *et al.* (1980); Garg and Ayoub (1980); NIOSH (1981/7); Westerling and Kilblom (1981); Ayoub (1982); AIHA (1983/5, 1989/16); Ayoub, Selan and Liles (1983); A.R. Hale (1984); Mital (1984a,b); Parnianpour, Bejjani and Pavlidis (1987); Nicholson (1989); Genaidy (1991); Snook and Ciriello (1991); Kroemer (1992); Pizatella *et al.* (1992); Waters *et al.* (1993); Kuorinka, Lortie and Gautreau (1994)

Machinery, machine guarding
BSC (n.d./5); HSE (HSW Bklt 4, 14, 20, 33, 42, TDN 32, 33, 38, 1970 HSW Bklt 41, 1971 HSW Bklt 3, 1980 MS 1, 1981 PM 21, 23, 1982 HS(G) 19, 1984 PM 1, 38, 1986 PM 65); Blackshield (1969); Bramley-Harker (1969); Fairclough (1969); S.F. Smith (1969); Harding (1977); Southwell (1977); R. King and Magid (1979); Kinsley (1980); Rouhianen (1982); Vartiala (1982)
ANSI B7.1–1988; BS (Appendix 27 *Machinery*)

Construction, demolition (see Table 21.1)

Welding (see Tables 12.1 and 21.1)

Abrasive wheels
Blackshield (1969); Southwell (1977); HSE (1984 HS(G) 17)

Pneumatic tools
PNEUPROP (n.d.a,b, 1986)

Miscellaneous hazards
American Oil Co. (n.d./1, 2, 6); MCA (SG-11); HSE (1971 HSW Bklt 27, 1974 HSW Bklt 46); FPA (1974 S8); BDH (1977c); Russell (1982)

Plant layout (see Table 10.2)

Lighting (see Table 10.2)

Identification and labelling (see also Table 23.1)
R.F. Wilson (1960); Gloag (1961); Hurst (1969); ASME (1975 A13.1–1975); MCA (1976/24); BDH (1977a); Stancliffe (1977); HSE (1985 HS(G) 27); API (1993 RP 1109)
BS (Appendix 27 *Identification of Equipment*)

Personal protection
NIOSH (1984/23, 1990/17); NRC (Appendix 28 *Personal Protective Equipment)*; N.T. Freeman (1962); H.H. Fawcett (1965b, 1982c); C.S. Nicholson (1969); W.I. Morton (1976); K.R. Nicholson (1976); Zippler (1976); Riddell (1977); Chlorine Institute (1978 Pmphlt 65); R. King and Magid (1979); BS (Appendix 27 *Personal Protection*)
Protective clothing, including gloves: ACGIH (n.d./10, 1989/30); Associated Octel Co. (1974 Bull. 21); Gauerke (1972); J.S. Shaw (1978); E.J. West *et al.* (1978); Crockford (1980); Stull (1987a,b); Hoyle (1988 LPB 80); Jones (1988 LPB 80); Parson (1988); Preece (1988); AIHA (1990/18); Mellin (1991 LPB 100); Tooth (1991 LPB 100); Bensel (1993); Pal *et al.* (1993); Mital, Kuo and Faard (1994)
Ear protection: Zohar, Cohen and Azar (1980)
Eye protection: Joyner (1959); Guelich (1965); Barker (1969, 1977); Wigglesworth (1974); Hill (1975); Nichols (1982); CIA (1990 RC22); ANSI Z87.1–1989; BS 2092: 1987
Footwear: FPA (1973 S4); ANSI Z41–1991; BS 1870: 1976–
Head protection: Anon. (1988 LPB 88, p. 14); ANSI Z89.1–1986; BS 5240: 1987–

Respiratory protective equipment, breathing apparatus
Fieldner, Katz and Kinney (1921); S.J. Pearce (1957); ACGIH and AIHA (1963); H.H. Fawcett (1965d, 1982d); Cheffers (1969); Home Office (1975 *Manual of Firemanship* Bk 6); Anon (1977–); Vanchuk (1978); HSE (1979 RA1); M.S. Levine (1979); Ballantyne and Schwab (1981); Chlorine Institute (1982 Pmphlt 75); Evans and Leinster (1984 LPB 60); IGasE (1986 IGE/SR/ 13); Louhevara *et al.* (1986); NIOSH (1987/12, 14); Anon. (1988 LPB 80); CGA (1989 G-7, G-7.1); HSE (1990 EH 53, HS(G) 53); Anon. (1991c); AIHA (1991/23); CIA (1991 RC6); Anon. (1992 LPB 106, p. 17); ACGIH (1992/ 88); ANSI Z88.2–1992; BS (Appendix 27 *Personal Protection*), BS 4275: 1974, BS 4667: 1974–, BS DD 97: 1987–, BS 7170: 1990, BS EN 132: 1991

Rescue
EEUA (1962 Doc. 12); Home Office (1964/8); Walters (1977); MoD (1989a); HSE (1992 RP23)
BS (Appendix 27 *Personal Protection, Rescue*)

First aid
HSE (HSW Bklt 36); St John Ambulance Association (1961, 1992); Gardner and Roylance (1967); Taylor (1967); Cameron (1969, 1977); API (1979 Publ. 2017); BDH (1977b); R. King and Magid (1979); McKenna and Hale (1981, 1982); Chlorine Institute (1985 Publ. 63); ACGIH (1988/19, 32, 1991/64)

Isolated workstations
Bresson and Perez (1977)

The general nature of the problem may be seen from the injury figures given in the *Health and Safety Statistics 1990/91* (HSE, 1992b) and shown in Table 25.2. These data refer to general industrial accidents and need to be supplemented for the chemical industry by data for that industry. These are reported on an occasional rather than an annual basis. Some accident data given in the *Annual Report* of HM Chief Inspector of Factories for 1985 are shown in Table 25.3.

The overall approach in questions of personal safety should always be, in order of descending preference, (1) hazard elimination, (2) hazard control and (3) personal protection. The principle of hazard elimination and control before resort to personal protection is a recurring theme.

Another recurring theme in personal safety is the need for thorough training and for effective supervision. The objectives of training should include not only the ability to use equipment and perform tasks, but also the understanding and motivation to do the work properly and safely. In other words, the worker should be convinced as well as instructed. Most of the hazards and activities described in this chapter have some training implications. The importance of training cannot be overemphasized. Similarly, it is essential to have good supervision so that malpractices are stopped and procedures are enforced.

25.1 Human Factors

Much can be done to reduce accidents by proper design of the work situation. This is the province of human factors. An account of human factors in general and of its application to the job of the process operator in particular is given in Chapter 14. Discussion here is confined to those aspects which are particularly relevant to personal accidents.

Guidance on human factors aspects is given in HS(G) 48 *Human Factors in Industrial Safety* (HSE, 1989). Further accounts are given in *Human Factors Engineering* (McCormick, 1957b), *Human Engineering Guide to Equipment Design* (C.T. Morgan *et al.*, 1963), *Human Engineering Guide for Equipment Designers* (Woodson and Conover, 1964), *Human Factors Evaluation in System Development* (Meister and Rabideau, 1965), *Ergonomics* (Murrell, 1965a), *Human Performance in Industry* (Murrell, 1965b), *Human Factors*

Table 25.2 *Injuries to employees by nature of accident and of injury and by severity of injury in the year 1990/91 (after HSE, 1992b)*[a]

A Nature of accident and severity of injury[b]

Nature of accident	*Severity of injury*		
	Fatal	*Non-fatal major*	*Total*
Contact with moving machinery or material being machined	29	1 738	9 491
Struck by moving, including flying or falling, object	51	2 371	25 788
Struck by moving vehicle	53	733	4 631
Struck against something fixed or stationary	3	781	11 074
Injured whilst handling, lifting or carrying	—	1 257	55 477
Slip, trip or fall on same level	1	6 396	39 849
Fall from a height:			
Up to and including 2 m	8	1 964	9 261
Over 2 m	66	1 337	3 162
Height not stated	7	973	4 517
All heights	81	4 274	16 940
Trapped by something collapsing or overturning	24	204	776
Drowning or asphyxiation	10	22	58
Exposure to or contact with a harmful substance	14	806	5 336
Exposure to fire	5	109	690
Exposure to an explosion	8	90	318
Contact with electricity or electrical discharge	24	298	929
Injured by an animal	3	72	928
Other kind of accident	28	651	7 960
Injuries not classified by kind	12	94	808
Total	346	19 896	181 053

B Nature and severity of injury[c]

Nature of injury	*Severity of injury*		
	Fatal	*Non-fatal major*	*Total*
Amputation	—	1 392	1 463
Loss of sight of eye	—	20	29
Fracture	46	14 108	27 035
Dislocation	—	30	1 146
Concussion and internal injuries	16	147	1 290
Lacerations and open wounds	3	617	12 453
Contusions	37	371	29 221
Burns	9	859	5 827
Poisonings and gassings	25	224	822
Sprains and strains	—	153	59 752
Superficial injuries	—	263	17 478
Natural causes	—	5	20
Other injuries caused by contact with electricity	19	80	318
Injuries of more than one of the other natures	37	261	2 738
Injuries not elsewhere specified	21	68	1 228
Injury not known	85	327	11 128
Total	298	18 925	171 948

[a] Source: Health and Safety Statistics 1990/91 (HSE, 1992b). Section A is an extract from Table 9 and Section B is an extract from Table 15.
[b] Injuries reported to all enforcing authorities, including offshore injuries.
[c] Injuries reported to the Factory and Agricultural Inspectorates and to local authorities.

(Meister, 1971), *Handbook of Human Factors* (Salvendy, 1987), *Applied Ergonomics Handbook* (Burke, 1992 ACGIH/76) and *Human Factors in Design and Engineering* (Sanders, 1993). Accounts of human factors with specific reference to safety are given in *Ergonomics Guides* (AIHA, 1970–/1), *Human Aspects of Safety* (Singleton, 1976b) and *Human Factors in Process Operations* (Mill, 1992) and by Hands (1969, 1977).

Human factors should be considered from the beginning of the project. Much of the contribution which it can make to accident prevention is in areas such as the allocation of function between man and machine. If it is brought in later for detailed equipment design or in a rescue role, many of the options for design are already foreclosed.

Much work in human factors is concerned with human error. In fact error rates are one of the main criteria used in scoring human factors experiments. Where an error leads to injury or other serious effect, it becomes an accident.

Error is to a large extent a function of the work situation. As such it is amenable to reduction by better design of the work situation, including not only equipment design but all other relevant factors. Some error is certainly attributable to the individual and variations in error rates between individuals can be investigated. But management should concentrate primarily on the work situation, since this is not only the factor which is most important but also that which it can most readily alter.

Principal influences on the frequency of errors, and hence of accidents, include (1) equipment design, (2) working methods, (3) motivation and (4) stress.

There is now a wealth of data on the design of equipment. The equipment should be physically easy to use. Valuable guidelines here are given by anthropometry, which is the study of human measurements.

It is often possible to build into equipment a barrier to error. A simple example is to prevent a plug being put into the wrong socket by making the relative shapes such that this is impossible. More complex methods for achieving similar results include interlocks.

Correct identification is important if error is to be avoided. There should be clear and consistent coding and labelling. A valuable form of coding is by colour.

Much information is available on the ways in which humans receive information through the senses. Some

Table 25.3 *Incidents in the chemical industry in 1983 (after HM Chief Inspector of Factories, 1986b)*

A Incidents

Incident type	*No. of incidents*	*Proportion of incidents* (%)
Releases of chemicals[a]	222	34.5
Machinery incidents	77	12.0
Process related fires and explosions	66	10.3
Falls from a height	56	8.7
Falls at same level and striking against objects	39	6.1
Pressure system and other equipment failures[b]	24	3.7
Hit by falling objects	23	3.6
Failure or overturning of lifting equipment	22	3.4
Struck or trapped by vehicle	15	2.3
Affected by chemicals during work[c]	13	2.0
Runaway exothermic reactions[d]	9	1.4
Manual handling and strains	8	1.2
Non-process related fires and explosions	7	1.1
Confined space incidents – people overcome	5	0.8
Electric short circuits	5	0.8
Not elsewhere classified	52	8.1
Total	643	100

B Other information

1. 17 incidents involved clear failures of the permit-to work system
2. There were 30 pipework failures in addition to 37 incidents involving flexible hoses or insecure temporary joints
3. Of the 222 releases of chemicals, 127 (57%) affected people directly or indirectly to some degree, 92 (41%) occurred during normal operation with no immediate direct involvement of workpeople, 64 (29%) occurred during normal operations with direct involvement of workpeople, 68 (30%) occurred during cleaning, maintenance or repair activities
4. 49 cases of ill health were recorded, mostly associated with the release of chemicals or with confined spaces
5. 17 incidents involved tanker vehicles or tank containers
6. 62 incidents (9.6%) involved personnel other than those employed by the occupier, i.e. contractors, visitors, etc.

[a] Including 97 toxic; 51 corrosive; 45 flammable; 23 hot, and 6 other materials.
[b] Where main risk was not from chemicals released.
[c] Examples are decanting, charging, etc., without significant escape or spill.
[d] With no major release of chemicals.

account of this has already been given in Chapter 14 in relation to the design of displays and controls.

It is necessary to train the operator in the use of equipment. The training should deal not only with how the operation is performed but also with why it is done that way.

Although training is important, it is not always the correct solution. Sometimes error is inherent in the design of the equipment. In this case it is better to redesign the equipment than to use training to overcome the defects.

It is important to pay attention to motivation in the use of correct and safe methods of operation, and this should be a major objective of training.

Human performance is much affected by stress. Some factors which cause this stress include poor environmental conditions, bad equipment design, lack of time, fatigue and anxiety. Although there tends to be some improvement in performance at moderate levels of stress, beyond a certain threshold (which is different for each individual) it causes severe deterioration.

Important aspects of the environment are air quality, thermal conditions, illumination and noise. The first two are considered in Section 25.3. The last two are treated by Ragsdale (1969) and Atherley and Purnell (1969). Noise is also dealt with in Appendix 12.

25.2 Occupational Health

Occupational health is an established branch of medicine. It involves not only the investigation of industrial disease, but also the provision of health services at the place of work.

Accounts of occupational health are given in *Occupational Diseases and Industrial Medicine* (R.T. Johnson and Miller, 1960), *Diseases of Occupations* (Hunter, 1975), *Occupational Health and Safety Concepts* (Atherley, 1978), *Recognition of Health Hazards in Industry* (Burgess, 1981 ACGIH/5), *Occupational Health* (Harrington and Gill, 1983–), *Chemical Exposure and Disease* (Sherman, 1988 ACGIH/16), *Occupational Health Practice* (Waldron, 1989), *Occupational and Environmental Health Management* (Kavianan and Wentz, 1990 ACGIH/47), *Health Fundamentals* (Hansen, 1991 ACGIH/71) and *Industrial Health* (Peterson, 1991 ACGIH/65). Epidemiological aspects are treated in *Exposure Assessment for Epidemiology and Hazard Control* (Rappaport and Smith, 1991 ACGIH/56) and *Introduction to Occupational Epidemiology* (Hernberg, (1992 ACGIH/79).

Guidance on occupational health arrangements is given in HS(G) 20 *Guidelines for Occupational Health Services* by the Health and Safety Executive (HSE) (1980).

25.2.1 Industrial medical services

A chemical works usually has a medical centre with facilities for medical tests and which is able to handle a small number of casualties. The centre is typically staffed by a doctor working part time and a nurse working shifts. Descriptions of such medical services and of their liaison with hospital emergency departments are given by Cameron (1969, 1977) and M.H. Hall (1969, 1977), respectively, and the work of an industrial nurse is described by Mort (1965).

The medical personnel should be familiar with the chemicals and processes used in the particular factory. Information such as that given on materials safety data sheets provides a useful starting point.

Information on the medical history of individual workers is equally important. Careful interviewing and record keeping can assist in diagnosing early symptoms or high susceptibility in individuals. It can also make a significant contribution to the epidemiological investigation of industrial disease.

25.2.2 Employment Medical Advisory Service

The Employment Medical Advisory Service Act 1972 and the Health and Safety at Work etc. Act (HSWA) 1974, Part II define the role of the Employment Medical Advisory Service (EMAS). Information on EMAS is given in *Employment Medical Advisory Service Act 1972—Guide to the Service*.

The service acts as the medical arm of the Health and Safety Commission (HSC), does work on medical matters for which there are statutory requirements, provides medical advice to the Factory Inspectorate and to employers, and furthers research on the epidemiology of industrial disease.

It is able to advise on the effects of particular jobs on health, on the medical precautions to be taken in working with substances which are toxic or otherwise hazardous to health, and on medical examinations, investigations and surveys.

There is a series of guidance notes on medical topics (the Medical Series (MS)) and also series of leaflets (the MS(A) and MS(B) series).

25.2.3 National Institute for Occupational Safety and Health

An important source of information on occupational health is the National Institute of Occupational Safety and Health (NIOSH). Some publications of the Institute are listed in Appendix 28.

25.3 Occupational Hygiene

Industrial chemicals tend to be noxious substances. It is essential, therefore, to take appropriate measures of occupational hygiene to ensure that those who work with them are not exposed to unacceptable risks.

Occupational health and hygiene are the subject of the Control of Substances Hazardous to Health Regulations 1988 (the COSHH Regulations). These are described together with the HSE guidance in Section 25.4.

Other regulations frequently referred to in this chapter are the Control of Lead at Work Regulations 1980 (the CLAW Regulations) and the Control of Asbestos at Work Regulations 1987 (the CAWR).

In addition to that specifically related to the COSHH Regulations 1988, HSE guidance includes EH 22 *Ventilation of the Workplace* (HSE, 1988), EH 42 *Monitoring Strategies for Toxic Substances* (HSE, 1989), HS(G) 61 *Surveillance of People Exposed to Health Risks at Work* (HSE, 1990), HS(G) 27 *Substances for Use at Work: the Provision of Information* (HSE, 1991) and EH 40/94 *Occupational Exposure Limits* (HSE, 1994).

Guidance by the British Occupational Hygiene Society (BOHS) is given in *Controlling Airborne Contaminants in the Workplace* (the BOHS *Airborne Contaminants Guide*) by Piney *et al.* (1987 BOHS/TG7) and by the American Industrial Hygiene Association (AIHA) in *Basic Industrial Hygiene: A Training Manual* (AIHA, 1975/2), *Engineering Field Reference Manual* (AIHA, 1984/7), and *A Strategy for Occupational Exposure Assessment* (Hawkins, Norwood and Rock, 1991 AIHA/24). A computer-based system is described in *LOGAN Workplace Evaluation System* (Dupont, 1990 AIHA/20).

Guidance on occupational hygiene in the petroleum industry is given in *Guidelines for Recording Industrial Hygiene Data* (CONCAWE, 1983 7/83), *Health Aspects of Worker Exposure to Oil Mists* (CONCAWE, 1986 86/69), *Review of Strategies for the Evaluation of Employee Exposures to Substances Hazardous to Health* (CONCAWE, 1987, 87/57) and *API Exposure Classification Scheme for Collection of Industrial Hygiene Monitoring Data* by the American Petroleum Institute (API, 1990).

Further guidance is given in *Employment and Reproductive Health* by the Chemical Industries Association (CIA) (1984 RC13).

Occupational, or industrial, hygiene is also treated in *Occupational Health and Safety Concepts* (Atherley, 1978), *Occupational Health* (Harrington and Gill, 1983–), *Case Studies in Industrial Hygiene* (Perkins and Rose, 1987 ACGIH/9), *Industrial Hygiene Management* (Garrett, Cralley and Cralley, 1988 ACGIH/23), *Fundamentals of Industrial Hygiene* by the National Safety Council (NSC) (1988/13), *The Risk Assessment of Environmental Hazards* (Paustenbach, 1989 ACGIH/37), *Quantitative Industrial Hygiene: A Formula Workbook* (Caravanos, 1991 ACGIH/74) and *Industrial Hygiene Workbook* (Burton, 1992 ACGIH/85). Engineering aspects are treated in *Health Hazards Control in the Chemical Process Industry* (Lipton and Lynch, 1987), *Industrial Hygiene Engineering* (Talty, 1988 ACGIH/22) and *In-Plant Practices for Job-related Health Hazards* (Cralley and Cralley, 1989 ACGIH/36).

Guidance for dusts specifically includes EH 44 *Dust: General Principles of Protection* (HSE, 1991), the *User Guide to Dust and Fume Control* (Muir, 1985) (the IChemE *Dust Control Guide*) and the BOHS *Airborne Contaminants Guide*.

The elements of occupational hygiene include:

(1) identification of noxious substances or effects;
(2) establishment of criteria;
(3) assessment of exposure;
(4) prevention of exposure;
(5) control of exposure –
  (a) enclosure,
  (b) ventilation;
(6) provision of personal protective equipment;
(7) monitoring of workplace atmosphere;
(8) monitoring of personnel;
(9) keeping of records.

This general approach is applicable to toxic and corrosive chemicals, noxious dusts, and ionizing and non-ionizing radiations.

In addition to vapours and dusts, it is necessary to deal also with skin disease and noise. Skin care is treated in Section 25.8 and noise is discussed in Appendix 12.

25.3.1 Noxious substances

Information on the health effects of industrial chemicals is available from a large number of sources. These include: *Dangerous Properties of Industrial Materials* (Sax, 1957–), *Hazardous Chemicals Handbook* (Carson and Mumford, 1994) and other compendia; *Chemical Safety Data Sheets* (Walsh, 1988, vol. 1) and (A. Allen (1988, other volumes); the series *Information Sheets on Hazardous Materials* by the Fire Protection Association (FPA) and other collections of such data sheets; and the Environmental Hygiene (EH) series and criteria documents (EH 64 and 65) by the HSE.

Information on hazardous chemicals, including materials safety data sheets, is discussed in Chapters 8 and 18, and materials toxicity in the latter chapter.

Some aspects of health effects in the petroleum industry are treated in *The Health Experience of Workers in the Petroleum Manufacturing and Distribution Industry* (CONCAWE, 1987 2/87) and *Survey of Exposure to Gasoline Vapour* (CONCAWE, 1987 4/87).

25.3.2 Airborne contaminants

A classification of airborne contaminants is given by the HSE (1993, HS(G) 37). The particle size ranges given are:

	Size range (μm)
Dusts	0.1–75
Fume	0.001–1.0
Smoke	0.01–1.0
Mist	0.01–10.0

These figures refer to: dust generated by natural fragmentation or mechanical cutting or crushing; fume formed as solid particles of condensed vapour, especially metals; smoke as aerosol formed by the incomplete combustion of organic matter; and mist as an aerosol of droplets formed by condensation from the gaseous state, or as a dispersion of the liquid state. For vapour a single value of 0.005 μm is quoted. This refers to the gaseous state of materials which are liquid or solid at room temperature and pressure.

The BOHS *Airborne Contaminants Guide* gives for contaminants of occupational importance a size range of 0.01–150 μm for both dust and mist, and of 0.001–1.0 μm for fume.

The particle size of a contaminant is determined by the process by which it is generated. Oil mist generated by metal cutting has a larger particle size that of oil fumes formed by the condensation of oil vapour.

The behaviour of an airborne particle may be characterized in terms of the settling velocity and the stopping distance. The latter is the distance which a particle with a defined initial velocity will travel before coming to rest. The BOHS *Guide*, quoting Hinds (1982), gives the following values for settling velocity and stopping distance:

Particle diameter (μm)	*Settling velocity* (m/s)	*Stopping distance* (m)
0.01	7.0×10^{-8}	6.8×10^{-8}
1.0	3.5×10^{-5}	3.6×10^{-5}
100	0.25	0.127

The particle density used is 10 kg/m^3 and the initial velocity for the stopping distance is 10 m/s.

Fine particles sediment out only very slowly and thus remain airborne for long periods. They move with the air.

Where particles are emitted from a source, the larger particles travel some distance, but the distance travelled by the finer particles is very short. Even if their initial velocity is high, their movement follows that of the air.

As far as concerns the health effects caused by particles, there is an upper limit of size above which a particle tends to be deposited before it reaches the lungs. The particle size range of interest for harmful effects by inhalation into the lungs is discussed in the BOHS *Guide*, which gives the range as being from the submicron level to about 25 μm in diameter.

25.3.3 Generation of contaminants

There is a variety of ways by which a contaminant may enter the workplace atmosphere. Four principal routes are (1) a contaminant-generating process or operation, (2) a leak, (3) opening up of plant and (4) handling fabrics saturated with the material.

For a vapour contaminant a principal determinant is the vapour pressure. If a liquid is being handled under conditions where there is a route to the atmosphere and it is at a temperature at which it exerts an appreciable vapour pressure, a significant amount may escape.

In relation to industrial hygiene a significant measure is the ratio of the vapour pressure to the occupational exposure limit. A vapour hazard index (VHI) is defined as

$$\text{VHI} = \frac{\text{Vapour pressure}}{\text{Occupational exposure limit}} \qquad [25.3.1]$$

where both the vapour pressure and the occupational exposure limit are measured in parts per million (ppm).

The conditions that must be met for a dust contaminant to enter the workplace atmosphere are that a route exists for it to do so and that it has imparted to it sufficient energy to follow that route.

Some conditions in which a contaminant, vapour or dust, may enter the atmosphere include (1) passage of air through the material, (2) free fall of the material, (3) pouring of the material, (4) agitation of the material, (5) transfer of the material, (6) opening of bags or drums of the material, (7) leak of the material, (8) opening up of plant containing the material and (9) handling of fabrics saturated with the material.

In addition, vapour generation may occur due to (1) the evaporation of a liquid or (2) the heating of a liquid; and dust generation may occur due to (1) vibration of a powder or (2) a size reduction of the material.

Typical equipment and activities where contaminants are generated include reactor charging, mixing operations, powder handling and packing processes, grinding mills, conveyors and elevators, storage silos, hoppers and

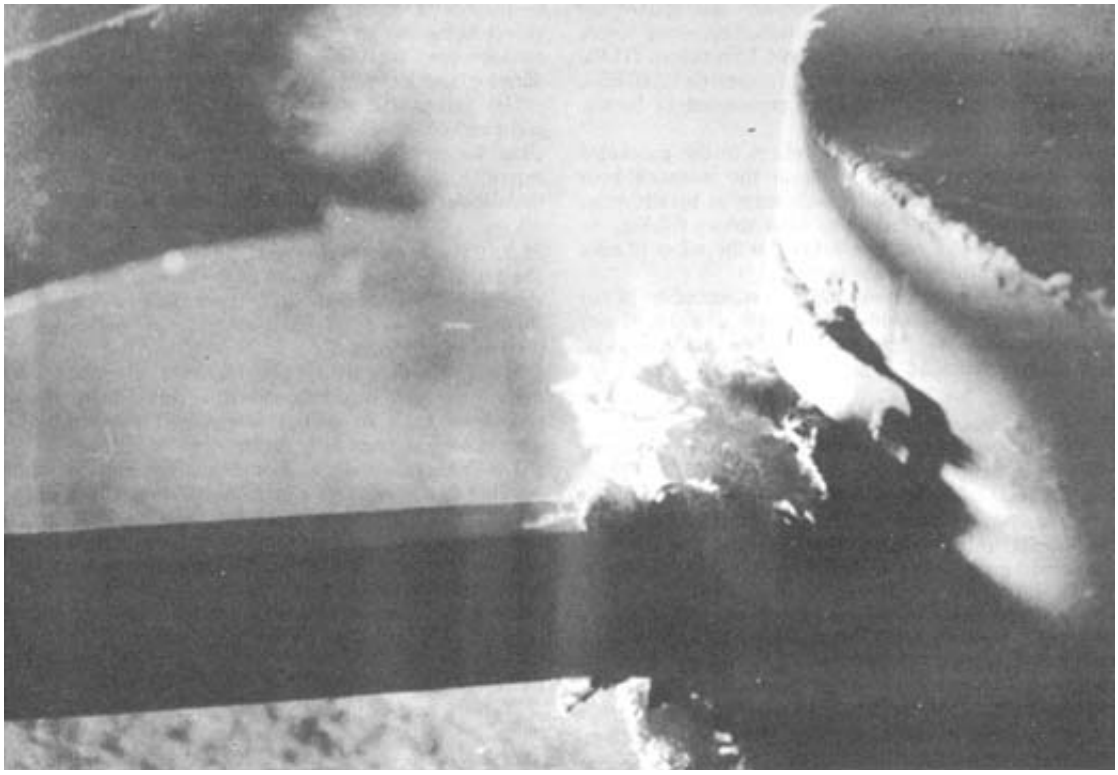

Figure 25.1 *Leakage of asbestos dust due to failure of a gaiter (HSE, 1975 TDN 35) (Courtesy of HM Stationery Office)*

bins, bag emptying operations, drum and bag filling operations, and plant maintenance.

The situations in which fumes and mists are generated tend to be highly specific.

25.3.4 Leaks of contaminants

A common source of contamination is leaks from the plant. A gross leak may be readily identified, but this may not be so where the leak is small, but still large enough to cause significant contamination.

With regard to leaks of gas, vapour and liquid, an account has been given in Chapter 15 of fugitive emissions, particularly of volatile organic compounds (VOCs). Although originally work on such emissions was driven largely by concern over environmental pollution, the information is generally applicable equally to emissions into the workplace atmosphere.

Leaks of dust can also occur. If the dust is fine, the leak may not be visible. Figure 25.1 shows a leak of asbestos dust from a gaiter, made visible only by the use of a dust lamp, as described below.

25.3.5 Air movement

As already described, most contaminants move with the air in the workplace. This air movement is therefore of great importance in developing controls.

There are available a number of methods for the investigation of air movements. One is the use of a smoke tracer. Smoke is introduced from a smoke generator and its movement is observed or filmed.

Methods exist for the visualization of the presence and movement of dust particles in air. The dust lamp, or Tyndall lamp, technique is widely used. This makes visible the dust cloud in a manner similar to that which occurs when a shaft of sunlight falls across a room where there is dust in the atmosphere. This method permits observation of dust clouds of particles too fine to be seen otherwise. The use of a dust lamp is illustrated in Figure 25.1. Accounts of the dust lamp technique are given by the HSE (1975 TDN 35) and in the *BOHS Guide*.

There is also an infrared technique which permits the movement of a vapour to be followed.

25.3.6 Monitoring variables and criteria

There is a hierarchy of methods which may be used as the basis for the monitoring and control of noxious substances. These are the measurement and monitoring of (1) the concentration of airborne contaminants in the workplace, (2) their concentration in workers' body tissues and body fluids and (3) their effect on workers' health.

There are three corresponding types of criteria used in monitoring for occupational hygiene. For the concentration of contaminants in the workplace atmosphere the criteria are expressed as occupational exposure limits. This type is exemplified by threshold limit values (TLVs) and occupational exposure standards (OESs). Occupational exposure limits are considered in Section 25.3.7.

The second type of criterion relates to the concentrations of toxic substances found in the worker's body tissues and fluids, especially fluids such as breath, urine and blood. These are biological limit values (BLVs).

The third type of criterion relates to the effect of toxic substances on the worker's health.

It should be emphasized that the concentration of any harmful substance should be kept not only below any maximum exposure limit but as close to zero as is reasonably practicable.

25.3.7 Occupational exposure limits

In the UK occupational exposure limits were formerly specified in terms of threshold limit values (TLVs). There are now two main types of limit which apply: occupational exposure standards (OESs) and maximum exposure limits (MELs). The latter apply to a relatively restricted group of chemicals which are listed in Schedule 1 of the COSHH Regulations 1988.

The larger group are covered by an OES. The current OES values are given in EH 40 *Occupational Exposure Limits* 1994 (HSE, 1994). The basis of the limits is explained in EH 64 *Occupational Exposure Limits: Criteria Document Summaries* (HSE, 1993).

An account of the OES system is given in *Occupational Exposure Limits* (CIA, 1985 PA23).

Further guidance is given by the AIHA in *Workplace Environmental Exposure Level Guides* (AIHA, 1980–/4), *Occupational Exposure Limits—Worldwide* (Cook, 1987 AIHA/12), *Hygienic Guides* (AIHA, 1988/14) and *Odor Thresholds for Chemicals with Established Occupational Standards* (AIHA, 1989/17). The American Conference of Government Industrial Hygienists (ACGIH) guidance includes *Documentation of the Biological Exposure Indices* (ACGIH/1), *Documentation of Threshold Limit Values and Biological Exposure Indices* (ACGIH/3), *Guide to Occupational Exposure Values—1992* (ACGIH/78) and *Threshold Limit Values and Biological Exposure Indices, 1992–1993* (ACGIH 1992/80). The International Labour Office (ILO) publishes *Occupational Exposure Limits for Airborne Toxic Substances* (ILO 1991/2).

25.3.8 Non-inhalation exposure

The account given so far has concentrated on exposure by inhalation. It is also necessary to consider exposure by ingestion and by skin absorption. The consumption of food and drink in contaminated conditions is one situation in which ingestion of a contaminant is prone to occur. Skin absorption is discussed in Section 25.8.

25.3.9 Assessment of exposure

If workers may be exposed to a noxious substance, an assessment needs to be made of the extent of the exposure. This assessment merits as much effort as is generally devoted to determining how noxious the substance is.

The foregoing account has indicated some of the processes, operations and activities which may cause contamination of the workplace atmosphere. The other aspect is the extent to which workers are exposed as a consequence of this contamination. The frequency, duration and intensity of exposure are all relevant.

The assessment should cover all modes of exposure and exposure due to activities as well as leaks. It should allow for foreseeable human behaviour. Assessment of exposure is an important aspect of the COSHH Regulations and is described further in Section 25.4.

25.3.10 Prevention of exposure

The minimization of exposure of workers to contaminants should be approached in a systematic manner and should be based on a hierarchy of measures of prevention and control.

In accordance with the philosophy of inherently safer design, the first objective should be prevention. Resort should be made to control only after the potential for prevention has been fully explored.

The prevention stage should address the following possible approaches: (1) elimination or substitution of the substance, (2) modification of the process, (3) segregation of processes, (4) elimination of leaks, (5) modification of operations and (6) arrangements for dealing with contaminated clothing.

Measures of prevention have two main objectives. One is to use substances which are less harmful. The other is to use processes and operations which are less prone to cause contamination.

In some cases it has proved possible to replace a harmful substance by substituting it by a less harmful one. In other cases the harmful substance may be eliminated. This may occur by elimination of a harmful impurity or of a process, or process stage, in which the harmful substance is used. Modification of the process by alteration or substitution is another approach which has been used with success. A third method is to segregate the processes, or process stages, which are 'dirty' in respect of contamination from those which are 'clean'. Examples of these approaches are given in Chapter 11 and in the BOHS *Guide*.

Where leaks are a cause of contamination, measures should be taken to eliminate them.

Contamination of the working atmosphere may also arise from various activities on the plant, such as opening reactors, taking samples or opening equipment up for maintenance. This aspect may need to be controlled by specific procedures.

Workers may be exposed to contamination from work clothes or from protective clothing, and arrangements may need to be made to prevent this.

25.3.11 Control of exposure

When measures based on prevention have been exhausted, controls should be used to reduce exposure further. These controls are applied in a hierarchy which is broadly as follows:

(1) total or partial enclosure;
(2) local exhaust ventilation;
(3) general ventilation;
(4) limitation of exposure –
    (a) number exposed,

(b) frequency and duration of exposure;
(5) personal protective equipment.

A further discussion of prevention and control is given in Section 25.4 in relation to the COSHH Regulations 1988.

25.3.12 Ventilation of workplace atmosphere

It is frequently necessary to use ventilation as one of the control measures taken to reduce exposure.

The siting of plant in the open air rather than in a building is often the most effective means of ventilation, since small leaks are then dispersed by the wind. But such open construction is not always appropriate, for various reasons, some of which were considered in Chapter 10. Moreover, as discussed below, it cannot be assumed that an outdoor location guarantees that exposure is negligible.

In most applications the preferred method of indoor ventilation is local exhaust ventilation. The use of general ventilation tends to be less effective and more expensive. Where general ventilation is used indoors, it may be natural ventilation or mechanical ventilation.

An account of ventilation is given in Section 25.7.

25.3.13 Monitoring of workplace atmosphere

The monitoring of the workplace atmosphere involves identifying valid methods of sampling, measurement and evaluation, and the adoption of a suitable monitoring strategy.

HSE guidance on the measurement and monitoring of contaminants in the workplace atmosphere is given in EH 42 *Monitoring Strategies for Toxic Substances* (HSE, 1989) and in the series *Methods for the Determination of Hazardous Substances* (MDHS). The series includes MDHS 70 *General Methods for Sampling Airborne Gases and Vapours* (HSE, 1990) and MDHS 71 *Analytical Quality in Workplace Air Monitoring* (HSE, 1991).

Further guidance by the AIHA is given in *Quality Assurance Manual for Industrial Hygiene Chemistry* (AIHA, 1988/15), *Direct-Reading Colorimetric Indicator Tubes Manual* (Perper and Dawson, 1993 AIHA/9), *The Industrial Hygienists' Guide to Indoor Air Quality Investigations* (AIHA, 1993/26), and *Manual of Recommended Practice for Combustible Gas Indicators and Portable Direct-Reading Health Survey Meters* (AIHA, 1993/27). ACGIH guidance includes *Methods of Air Sampling and Analysis* (Lodge, 1988 ACGIH/24), *Air Sampling Instruments* (ACGIH, 1989/27) and *Air Monitoring for Toxic Exposures* (Ness, 1991 ACGIH/51).

For petroleum products the guidance available includes *The Identification and Measurement of Refinery Odors* (CONCAWE, 1975 8/75) and *Method for Monitoring Exposure to Gasoline Vapour in Air* (CONCAWE, 1986 8/86).

Strategies for measuring and assessing personal exposure are described in *Review of Strategies for the Evaluation of Employee Exposure to Substances Hazardous to Health* (CONCAWE, 1987 87/57).

25.3.14 Health surveillance

It may not be sufficient to monitor the working atmosphere. It is often necessary also to monitor the people who work in it by a system of health surveillance. HSE guidance on health surveillance is given in HS(G) 61 *Surveillance of People Exposed to Health Risk at Work* (HSE, 1990).

HS(G) 61 lists the sets of regulations which contain requirements for medical surveillance. They include the CLAW Regulations, the CAWR and the COSHH Regulations.

Health surveillance may be carried out at different stages of an employee's involvement with the company. HS(G) 61 distinguishes between the types of surveillance which occur during recruitment, on employment, during work and on detection of an adverse effect.

HS(G) 61 gives the following purposes of health surveillance at work: (1) to identify adverse effects early, (2) to identify inadequacies in control, (3) to inform those at risk as soon as possible of any damage to their health and (4) to provide an opportunity to reinforce health education on the risk present.

It also describes some of the practicalities. (1) There are some substances which it is impractical to control to a level which protects all those who may be exposed, due to differences in the susceptibility of individuals. A person sensitized to a lung allergen may develop asthma at a concentration level three orders of magnitude lower than would affect a previously unexposed person. (2) Control may not be equally effective in protecting all groups of workers. Controls designed to protect plant operators may well not cover maintenance personnel. (3) The controls may not do all they were intended to do. Early controls on cotton dust did not prevent byssinosis, because they did not remove fine particles. (4) The type of injury may not be foreseen. This was the case with lung cancers from asbestos up to about 1940 and with mesothelioma from vinyl chloride monomer until about 1974.

Employees should be informed of possible consequences of health surveillance. One potential consequence might be that an employee is moved to another job.

As with monitoring of exposure to airborne contaminants, so with monitoring of concentrations of toxic substances in the body, the aim should be to keep the concentrations as low as is reasonably practicable.

Guidance on monitoring against biological limit values is given by the ACGIH in *Biological Monitoring of Exposure to Chemicals: Organic Compounds* (Dillon and Ho, 1987 ACGIH/8), *Methods for Biological Monitoring* (Knelp and Crable, 1988 ACGIH/25) and *Biological Monitoring of Exposure to Chemicals: Metals* (Dillon and Ho, 1991 ACGIH/52). AIHA guidance includes *Biohazards Reference Manual* (AIHA, 1985/10).

25.3.15 Hot environments

The environment may also be injurious to health because it is too hot. This aspect is treated in *Hot Environments* (NIOSH, 1986 Publ.86–113) and by Bedford (1974) and Gill (1980a).

Depending on the situation, countermeasures for hot environments may include the provision of ventilation, the use of protective clothing and the limitation of the working period.

25.4 COSHH Regulations 1988

A requirement for a comprehensive system for the protection of workers based on industrial hygiene

Table 25.4 *Principal contents of the Control of Substances Hazardous to Health Regulations 1988 and the associated Guidance*

Regulation 2	Interpretation
Regulation 3	Duties under these Regulations
Regulation 4	Prohibitions relating to certain substances
Regulation 6	Assessment of health risk created by work involving substances hazardous to health
Regulation 7	Prevention or control of exposure to substances hazardous to health
Regulation 8	Use of control measures, etc.
Regulation 9	Maintenance, examination and test of control measures
Regulation 10	Monitoring exposure at the workplace
Regulation 11	Health surveillance
Regulation 12	Information, instruction and training for persons who may be exposed to substances hazardous to health
Schedule 1	List of substances assigned maximum exposure limits
Schedule 2	Prohibition of substances hazardous to health for certain purposes
Schedule 3	Frequency of thorough examination and test of local exhaust ventilation plant used for certain processes
Schedule 4	Specific substances and processes for which monitoring is required
Schedule 5	Medical surveillance
Appendix	Health records

principles is given in the Control of Substances Hazardous to Health Regulations 1988 (the COSHH Regulations). The corresponding Approved Code of Practice (ACOP), which deals also with carcinogenic substances, is L5 (formerly COP 29) *Control of Substances Hazardous to Health and Control of Carcinogenic Substances* (HSE, 1991). It is convenient to refer to these two parts of the ACOP as the *COSHH Code* and the *Carcinogens Code*, respectively. Further guidance is given in *COSHH Assessments* (HSE, 1988b), HS(G) 27 *Substances for Use at Work: the Provision of Information* (HSE, 1988), EH 42 *Monitoring Strategies for Toxic Substances* (HSE, 1989) and HS(G) 61 *Surveillance of People Exposed to Health Risks at Work* (HSE, 1990).

Guidance from the CIA is given in the series *COSHH—Guidance on Assessments (Reg. 6)* (CIA, 1989 RC9), *COSHH—Guidance on Health Surveillance (Reg. 11)* (CIA, 1989 RC11), *COSHH—Guidance on Information, Instruction and Training (Reg. 12)* (CIA, 1990 RC 12), *COSHH—Guidance on Setting In-house Exposure Limits (Reg. 7)* (CIA, 1990 RC10), *COSHH—Guidance on Collection and Evaluation of Hazard Information (Reg. 2)* (CIA, 1991 RC39) and *COSHH—Guidance on Recordkeeping* (CIA, 1991 RC 38).

Further treatments are given in *The COSHH Regulations: A Practical Guide* (Simpson and Simpson, 1991) and by P. Lewis (1980), Blain (1987), Waterman (1987) and Boniface (1990b). The principal contents of the COSHH Regulations are given in Table 25.4.

Regulation 2 defines a 'substance hazardous to health' (SHH) as covering the following: (1) a substance which is listed in Part 1A of the Classification, Packaging and Labelling of Dangerous Substances Regulations 1984 and for which the general indication of nature of risk is specified as very toxic, toxic, harmful, corrosive or irritant; (2) a substance for which the maximum exposure limit is specified in Schedule 1 of the regulations or for which the HSC has approved an occupational exposure standard; (3) a micro-organism which creates a hazard to health; (4) dust of any kind, when present at a substantial concentration in air; and (5) any other substance which creates a comparable hazard to health.

The regulations cover substances which have chronic or delayed effects such as substances which are carcinogenic, mutagenic or teratogenic.

Under Regulation 3 an employer has towards an employee the duties of: (1) assessment; (2) prevention or control of exposure; (3) use of control measures and their maintenance, examination and test; (4) provision of information and training; and, where appropriate, (5) monitoring of workplace exposure; and (6) health surveillance. So far as is reasonably practicable, the employer should regard himself as having similar duties towards other persons at the premises, except that there is no duty of health surveillance, and as having the first three duties listed towards others likely to be affected by the work. These duties are not confined to the occupier but apply also to contractors. Thus the duties of an employer are owed by a contractor to his employees.

Regulation 4 places prohibitions on certain substances listed in Schedule 2 to the extent specified in that schedule. This includes a prohibition on: the manufacture and use of 2-naphthylamine, benzidine, 4-aminodiphenyl and 4-nitrodiphenyl; the use of benzene for any purpose other than in an industrial process; and on the use of sand for sand blasting.

Regulation 6 requires that the employer make 'a suitable and sufficient assessment' of the risks created by the work and of the steps which need to be taken to ensure compliance. The assessment should be reviewed if there is reason to suspect that it is no longer valid or if there has been a significant change in the work.

Regulation 7 requires that exposure to substances hazardous to health should be prevented or, where this is not reasonably practicable, adequately controlled. Further, it requires that so far as is reasonably practicable this be done without recourse to personnel protective equipment, but that where necessary such equipment should be provided. Where a substance has a maximum exposure limit specified in Schedule 1, the exposure should not exceed this limit and should be reduced below it to the extent which is reasonably practicable. Where a substance has an occupational exposure standard, the exposure should not exceed this standard, but if it does the employer should identify the reason and take action to remedy the situation as soon as is reasonably practicable. The exposure referred to may be any route, including inhalation, ingestion, absorption through the skin or contact with it.

Regulation 8 requires that an employer providing any control measure, personal protective equipment or other

item, should take all reasonable steps to see that these are properly applied and that an employee should apply them and report any defects.

Regulation 9 requires adequate maintenance, examination and test of control measures. It refers specifically to local exhaust ventilation and to respiratory protective equipment. For the former it lays down a maximum interval for examination and test of 14 months or, for plant specified in Schedule 3, the interval given in that schedule. It requires that a record be kept of the examination and test, and of any repairs effected.

Regulation 10 requires that, where necessary to ensure control of exposure or prevent harm, monitoring of the workplace should be carried out using a suitable procedure. For certain substances given in Schedule 4 monitoring is required at the minimum frequency specified in the schedule. The regulation requires that records, or suitable summaries, be made and that where they are representative of the personal exposure of identifiable employees they should be kept for 30 years.

Regulation 11 requires that, where it is appropriate for the protection of the health of employees who are liable to be exposed to a substance hazardous to health, the employer should set up a system of health surveillance. The regulation is a long one, with some 12 sections. Regulation 11(2) states that health surveillance is appropriate where the employee is exposed to one of the substances and is engaged in one of the processes listed in Schedule 5, unless the exposure is insignificant, or where he is exposed to a substance so that an identifiable disease or adverse health effect may be related to the exposure, there is a reasonable likelihood that the disease or effect may occur given the conditions of his work, and there is a valid technique for detecting indications of the disease or effect.

Regulation 12 requires the employer to provide to an employee who does work which may expose him to a substance hazardous to health such information, instruction and training as is suitable and sufficient for him to know the risks to health and the precautions to be taken. The information should include the results of any monitoring carried out in compliance with Regulation 10. If, in the case of a substance listed in Schedule 1, the maximum exposure limit is exceeded, the employee should be informed immediately. The information should also include the collective results of any health surveillance carried out in compliance with Regulation 11, presented in a form where the data cannot be related to a particular individual.

Regulation 12(3) requires that any person, whether or not an employee, who carries out work in connection with the employer's duties under the COSHH should have the necessary information, instruction and training.

Regulation 6 requires that the person making the assessment be competent and refers to Regulation 12(3).

25.4.1 Substances hazardous to health

There are a number of factors mentioned in the ACOP which need to be borne in mind when considering whether a substance is hazardous to health. The same substance may be hazardous in one form but not in another. Thus a substance in dust form may be hazardous but be safe in solid form. The fibrous form may also be hazardous. A substance may contain an impurity which is more hazardous than the substance which it contaminates. A substance may have been found by experience to be hazardous, even if the causative agent has not been identified. Some combinations of substances may have harmful additive, or synergistic, effects.

25.4.2 Suitable and sufficient assessment

The ACOP states that the purpose of the assessment is to obtain the information necessary to select suitable control measures. It also provides a demonstration that the relevant factors have been taken into account and the measures necessary taken.

A suitable and sufficient assessment should include an assessment of the risks to health, a determination of the measures which need to be taken to achieve control under Regulation 7, and an identification of any other action necessary to comply with Regulations 8–12.

The assessment of risks should identify the substances to which personnel are liable to be exposed, the effects of the substances on the body, the places where and the forms in which these substances are likely to be present, and the ways in which and the extent to which personnel could be exposed, allowing for foreseeable deterioration, or failure, of a control measure. It should include an estimate of the exposure given the engineering measures and systems of work adopted. This estimate should be compared with any available standards for adequate control.

If comparison indicates that control is likely to be inadequate, the assessment should go on to determine the measures which need to be taken to achieve adequate control. A record should be kept of the assessment, except in very simple and obvious cases which could be readily repeated and explained at any time.

The assessment should be reviewed if it is shown to be no longer valid by some new information, which may include: results from the periodic examination and test of the engineering controls; results from the monitoring of workplace exposure; results of health surveillance, or a confirmed case of occupationally induced disease; or new information on health risks. A review is also called for if there is a significant change in the work, including any change in the substances used, the process, the throughput, the work practices or the engineering controls.

Further guidance on the assessment is given in *COSHH Assessment*. The stages of the assessment are the gathering of information, the evaluation of the risks, the specification of the measures and precautions required and the recording of the assessment. Information needs to be gathered on the substances and their hazards and on the work and the working practices.

Evaluation of the risks from a substance involves assessing, on the one hand, the potential for harm from exposure to it and, on the other, the nature of any exposure. For the latter, it is necessary to determine the situations in which exposure may occur, the persons liable to be exposed, and the frequency and duration of exposures.

Where there is uncertainty about the magnitude or significance of the exposure in relation to the requirement for prevention or adequate control, exposure should be measured, provided there is a suitable method of measurement.

COSHH Assessment identifies five possible outcomes of the assessment, which may be summarized as:

(1) risks are insignificant now and for the foreseeable future;
(2) risks are high now, and not adequately controlled;
(3) risks are controlled now, but foreseeably could become higher;
(4) risks are uncertain – uncertainty concerns extent and degree of exposure;
(5) risks are uncertain – uncertainty due to lack of information.

Guidance is given on the action to be taken for each of these outcomes.

25.4.3 Competent person

COSHH Assessment also gives guidance on the competence required of the person who is to undertake the assessment. The guide distinguishes between basic skills and additional skills. The basic skills are an understanding of the regulations and the abilities to make a systematic assessment of the risks and the exposures, to specify the measures which need to be taken in the light of the assessment, and to communicate the findings in a report.

The additional skills are qualifications, experience and training. The guide emphasizes particularly practical experience and an understanding of the behaviour of people as well as processes.

25.4.4 Occupational exposure limits

As already stated, the two types of occupational exposure limit mentioned in the regulations are the maximum exposure limit (MEL) and the occupational exposure standard (OES). The MELs are listed in Schedule 1 and the OESs are contained in the List of Approved OESs. This is given in EH 40 *Occupational Exposure Limits*, which is up-dated annually.

The status of these two exposure limits is described in the ACOP. A MEL is the maximum concentration to which an employee may be exposed by inhalation under any circumstances. The concentration is averaged over a reference period which is specified in Schedule 1. Further details of the application of MELs are given in the ACOP.

Where an OES is assigned, exposure should be reduced to that standard. However, if exposure by inhalation exceeds the OES, the control may still be deemed adequate provided the reason for the excursion has been identified and appropriate steps are being taken to comply with the OES as soon as is reasonably practicable.

Where a substance is not assigned an MEL or OES, the ACOP states that the concentration should be controlled to a level to which nearly all the population could be exposed, day after day, without adverse effects on health.

25.4.5 Measurement and monitoring

The ACOP states that compliance with an OES may be demonstrated by measuring and recording the exposure of employees in accordance with EH 42 *Monitoring Strategies for Toxic Substances* (HSE, 1989).

Guidance is given in the ACOP on those situations where monitoring is required. Paragraph 68 states that it is always required for substances in Schedule 4 and, in addition, unless it is immediately obvious that control is adequate or suitable procedures for monitoring do not exist and cannot be devised, the requirement exists (1) where failure or deterioration of the control measures could result in a serious health effect, either because of the toxicity of the substance or the extent of the potential exposure, or both, (2) where measurement is necessary to ensure that a MEL or OES or any self-imposed working standard is not exceeded or (3) an additional check is required on the effectiveness of any control measure required under Regulation 7.

EH 42 gives detailed advice on such monitoring, including sampling strategies and interpretation of results.

25.4.6 Prevention and control

The ACOP states that adequate control is achieved if certain standards set out in paragraphs 27–30 of the code are met. Paragraph 27 deals with substances assigned an MEL, paragraph 28 with substances assigned an OES, paragraph 29 with other inhaled substances and paragraph 30 with exposure by routes other than inhalation. Compliance with an OES may be demonstrated by monitoring, as just described.

As far as is reasonably practicable, prevention or adequate control of exposure should be achieved by means other than personal protective equipment. Circumstances in which it may be necessary to resort to the latter include those: (1) where it is not technically feasible to achieve adequate control by process, operational and engineering measures alone; (2) where a new or revised assessment necessitates the temporary use of personal protection until adequate control is achieved by other means; (3) where urgent action is required, such as that following a plant failure; and (4) where routine maintenance operations have to be done. In deciding whether to use personal protective equipment, due allowance should be made for its limitations and the practicalities of its use.

The ACOP enumerates the measures which may be used for the prevention or control of exposure to a substance hazardous to health. Prevention may be effected by elimination of the substance or by substitution of a less hazardous substance. Twelve measures are listed for control: (1) a totally enclosed process and handling system; (2) a plant, process or system of work which minimizes the generation of, or suppresses or contains, fumes, dusts, etc.; (3) a partially enclosed system, with local exhaust ventilation; (4) local exhaust ventilation; (5) sufficient general ventilation; (6) a reduction of the number workers exposed and a restriction of access; (7) a reduction in the period of exposure; (8) regular cleaning of surfaces and walls; (9) the provision of a means of the safe storage and disposal of the substance; (10) suitable personal protective equipment; (11) prohibition of eating, drinking and smoking in contaminated areas; and (12) provision of adequate facilities of washing, changing and storage of clothing, including laundry arrangements for contaminated clothing.

25.4.7 Personal protective equipment

Personal protective equipment (PPE) includes respiratory equipment, protective clothing, footwear and eye protection. The selection of such equipment for protection against a substance should take into account the ability of the material to resist penetration by the substance, the adequacy of the design of the clothing and its suitability for the intended use, the environment in which it is to be worn, and, in the case of dust, the dust release characteristics of the material.

25.4.8 Health surveillance

Guidance on health surveillance is given in the ACOP and also in HS(G) 61 *Surveillance of People Exposed to Health Risks at Work* (HSE, 1990). The ACOP describes the purposes of health surveillance, the type of surveillance suitable and the situations in which it should be undertaken.

The purposes of health surveillance are essentially the protection of the health of employees and the evaluation of health hazards and control measures. The surveillance should lead to action and, before it is undertaken, the options and criteria should be established.

The health surveillance procedures enumerated in the ACOP are: (1) biological monitoring; (2) biological effect monitoring; (3) medical surveillance; (4) enquiries about symptoms, inspection or examination by a suitably qualified person; (5) inspection by a responsible person; and (6) a review of the records and occupational history during and after exposure. Biological monitoring is based on the measurement of agents or their metabolites in body tissues or fluids, whilst biological effect monitoring is based on the biological effects on the worker. In this context, a suitably qualified person is instanced as an occupational health nurse and a responsible person as a manager or supervisor. The latter might check, for example, for chrome ulceration.

Health surveillance is appropriate for any exposure which fulfils the criteria of Regulation 11(2). The judgement on the likelihood of disease or adverse effects should be related to the nature and degree of exposure and should take into account information on epidemiology, human exposure, human and animal toxicological data, as well as extrapolation from information about analogous substances or situations.

25.4.9 Schedule 5

Frequent reference has been made in the foregoing to Schedule 5. This contains in Column 1 the names of various substances and in Column 2 processes in which they are involved.

One substance listed in this schedule is vinyl chloride monomer (VCM). The processes given in Column 2 opposite this substance are manufacture, production, reclamation, storage, discharge, transport, use or polymerization.

25.4.10 Carcinogenic substances

The ACOP contains a second, separate section, or code, covering the control of carcinogenic substances (the *Carcinogens Code*). The *Carcinogens Code* covers scope, prohibitions, assessment, prevention and control, monitoring, health surveillance and information, instruction and training. Its structure thus reflects that of the COSHH Regulations and code. It is an amplification of the *COSHH Code* and not a replacement for it.

With regard to scope, the code applies to substances assigned the 'risk phrase' 'R45: May cause cancer' of the Classification, Labelling and Packaging Regulations 1984 and listed in Part IA1 of the approved list and to substances listed in Appendix 1 and substances arising from processes listed in that appendix. Certain substances are prohibited and these are listed in Schedule 2.

The guidance on assessment and on prevention and control largely follows that of the *COSHH Code*, but there are certain particular emphases and specific measures.

Exposure to a carcinogen involves a risk of cancer. The risk increases with the exposure but there may be no short-term manifestation of adverse effects. The dose–response relation is quantal rather than graded.

In the case of carcinogens particular importance attaches to prevention. The use of carcinogenic substances should be kept to a minimum, these should be clearly labelled, and the areas where they are used should be delineated and non-essential personnel excluded.

The first choice for control should be a totally enclosed system. Where this is not practical, alternative effective engineering measures should be taken including, where appropriate, the use of local exhaust ventilation. Care needs to be taken, however, that control measures do not aggravate the risk in the workplace or the outside environment.

Since exposure to carcinogens can result in a serious health effect, monitoring is normally required under paragraph 68 of the *COSHH Code*.

The *Carcinogens Code* states that, unless exposure is insignificant, health surveillance is appropriate for all carcinogenic substances. For substances in Schedule 5 of the regulations, medical surveillance is required. The code explains the objectives and limitations of surveillance. Surveillance has limitations in the identification of susceptible persons and in early recognition of cancer. It is largely restricted to the keeping of records to protect workers through the detection and evaluation of health risks.

In view of the nature of the risk, workers who may be exposed should be given full information about it and on the importance of prevention, control and hygiene measures. This should include information on the long-term risk and on the need for continued surveillance.

25.5 Dust Hazards

In general industry, dust is one of the most serious hazards to health. Even in the chemical industry, where there are many toxic vapours, dust remains a relatively important airborne contaminant.

The HSE guidance on dust hazards and their control is given in *Principles of Local Exhaust Ventilation* (HSE, 1975a), MS 4 *Organic Dust Surveys* (HSE, 1977), EH 44 *Dust: General Principles of Protection* (HSE, 1991) and EH 40/94 *Occupational Exposure Limits* 1994 (HSE, 1994). Further guidance is given in *User Guide to Dust and Fume Control* (Muir, 1985) (the IChem *Dust Control Guide*), the *BOHS Airborne Contaminants Guide* and *Dust Control Handbook* (Mody and Jakhete, 1988 ACGIH/18) and by Bridgwater (1983).

25.5.1 Health effects of dusts

Some dusts have harmful effects, and some of the most harmful airborne contaminants are dusts. There are many dusts, however, which are inert, although they are unpleasant to breathe. Some account of the effects of dust on health and of exposure limits is given in Chapter 18.

EH 40 requires that, in the absence of a specific exposure limit for a particular dust, exposure should be kept below both 10 mg/m^3 8-hour time-weighted average (TWA) total inhalable dust and 5 mg/m^3 8-hour TWA total respirable dust. Respirable dust is the fraction of inhalable dust which penetrates to the lung.

Much the most important harmful effect from dusts is the various forms of fibrosis such as silicosis from silica or asbestosis from asbestos dust. Metals which are essentially harmless in bulk form may have dusts which are to some degree toxic and cause severe lung inflammation. Some dusts are associated with lung cancer.

25.5.2 Measurement of dusts

As described earlier, techniques exist for the visualization of dust clouds so that the presence and movement of dust in the workplace atmosphere may be followed. Such visualization is often sufficient to check the general state of the atmosphere, to detect leaks and to investigate the effectiveness of measures for dust suppression.

However, if the concentration of the dust is to be controlled in accordance with exposure limits, then a quantitative measurement of the total particle concentration is needed. It may also be necessary to measure the particle size distribution. The measurement of particle concentration and size distribution is a specialist matter.

Methods for the sampling and measurement of dust in air are described in the IChemE *Dust Control Guide*, the BOHS *Airborne Contaminants Guide, Particle Size Analysis* (Lloyd, 1987) and *Particle Size Analysis* (Stanley-Wood and Lines, 1992), and by Stairmand (1951), T. Allen (1975), Munns (1977), Kaye (1981), Vincent and Mark (1981) and Rood (1992a,b).

25.5.3 Minimization of exposure to dusts

The general approach to the minimization of exposure is similar to that taken for airborne contaminants generally and is described in Section 25.3, which makes frequent reference to dusts.

Section 25.3 describes the generation of dusts and methods for the prevention and control of exposure. Amplifying these as regards prevention, there are a number of industrial examples of the elimination of dust by such means as the substitution of different materials or a change of process. The substitution of metal shot for silica sand in shot blasting eliminates silica dust. The change from dry to wet processes for asbestos products largely eliminates asbestos dust.

Another important aspect of prevention is the suppression of dust fines. Here one approach is to prevent the generation of fines by a modification of material or process. This is exemplified by the use of spray drying or fluidized bed processes to produce granular products. Another approach is the use of a de-dusting agent. This finds application in the treatment of many pigments with very small amounts of liquid de-dusting agent.

Where exposure cannot be reduced sufficiently by prevention, it is necessary to resort to control. The methods of control available are described in Section 25.3. These include in particular enclosure and local exhaust ventilation (LEV). Indeed, accounts of LEV are couched mainly in terms of the control of dusts.

Good housekeeping and hygiene measures assume particular importance for dusts, especially highly toxic dusts. The objective of good housekeeping is to prevent dust from being carried back into the atmosphere. It includes the construction of buildings to eliminate dust-collecting surfaces and permit easy cleaning, the avoidance of dust spillages, the removal of dust piles and of pastes which form dust when dried, and the cleaning of dust-collecting surfaces. Arrangements to prevent contamination by dusty clothing may also be necessary.

25.6 Asbestos Dust

Asbestos dust is a particularly important hazard and occurs in the process industries. It is appropriate, therefore, to give it separate consideration. The effect of asbestos dust on health was described in Chapter 18 and it is principally the control of the dust which is considered here.

The relevant regulations are the Control of Asbestos at Work Regulations 1987 (CAWR). There are two ACOPs, L27 (formerly COP 21) *Control of Asbestos at Work* (HSE, 1993) and COP 3 *Work with Asbestos Insulation, Asbestos Coating and Asbestos Insulation Board* (HSE, 1988).

Further guidance on asbestos dust is given in EH 10 *Asbestos: Exposure Limits and Measurement of Airborne Dust Concentrations* (HSE, 1990). There are a number of other guidance documents from the HSE, including MS 13 *Asbestos* (HSE, 1988), EH 41 *Respiratory Equipment for Use Against Asbestos* (HSE, 1985), EH 50 *Training Operatives and Supervisors for Work with Asbestos Insulation and Coatings* (HSE, 1988), EH 51 *Enclosures Provided for Work with Asbestos Insulation, Coatings and Insulating Boards* (HSE, 1989), EH 35 *Probable Asbestos Dust Concentrations at Construction Processes* (HSE, 1989), EH 52 *Removal Techniques and Associated Waste Handling for Asbestos Insulation, Coatings and Insulation Boards* (HSE 1989), EH 37 *Work with Asbestos Insulating Board* (HSE, 1989), EH 47 *Provision, Use and Maintenance of Hygiene Facilities for Work with Asbestos Insulation and Coatings* (HSE, 1990) and EH 36 *Work with Asbestos Cement* (HSE 1990).

A US viewpoint is given in *Asbestos: Medical and Legal Aspects* (Castleman, ACGIH 1990/39).

The principal contents of the CAWR are given in Table 25.5. It can be seen from this table that the general structure of the CAWR mirrors that of the COSHH Regulations, with requirements for the assessment, prevention or reduction of exposure, control measures, maintenance of control measures, air monitoring, health records and medical surveillance, and information, instruction and training. The CAWR also contain, however, a number of other provisions which are described below and which serve as an additional model for exposures of this general type.

Regulation 4 requires that the type of asbestos to which exposure may occur be identified.

Regulation 2 defines action levels and control limits. The action levels are 96 fibre-hours/ml of air where

Table 25.5 *Principal contents of the Control of Asbestos at Work Regulations 1987 and the associated Guidance*

Regulation 2	Interpretation
Regulation 3	Duties under these Regulations
Regulation 4	Identification of the type of asbestos
Regulation 5 and 5A	Assessment of work which exposes employees to asbestos
Regulation 6	Notification of work with asbestos
Regulation 7	Information, instruction and training
Regulation 8	Prevention or reduction of exposure to asbestos
Regulation 9	Use of control measures, etc.
Regulation 10	Maintenance of control measures, etc.
Regulation 11	Provision and cleaning of protective clothing
Regulation 12	Duty to prevent or reduce spread of asbestos
Regulation 13	Cleanliness of premises and plant
Regulation 14	Designated areas
Regulation 15	Air monitoring
Regulation 16	Health records and medical surveillance
Regulation 17	Washing and changing facilities
Regulation 18	Storage, distribution and labelling of raw asbestos and asbestos waste
Regulation 19	Supply of products containing asbestos for use at work
Schedule 1	Particulars to be included in a notification

exposure is solely to chrysotile, and 48 fibre-hours/ml of air where exposure is to any other form of asbestos alone or in mixtures including mixtures of chrysotile with any other forms of asbestos. Where both types of exposure occur separately over a 12-week period, a proportionate number of fibre-hours per ml of air applies.

The control limits given in this regulation are for chrysotile (1) 0.5 fibres/ml of air averaged over any continuous period of 4 hours and (2) 1.5 fibres/ml of air averaged over any continuous period of 10 minutes. For any other form of asbestos either alone or in mixtures, including mixtures of chrysotile with any other forms of asbestos, the control limits are (1) 0.2 fibres/ml of air averaged over any continuous period 4 hours and (2) 0.6 fibres/ml of air averaged over any continuous period of 10 minutes.

In general, the regulations apply to any exposure to asbestos at work, but some particular regulations are triggered only if exposure is liable to exceed the action level. These are Regulations 6, 14 and 16, relating, respectively, to notification, designated areas and medical surveillance.

Regulation 6 requires notification of work with asbestos unless the exposure is not liable to exceed the action level or the employer is licensed under the Asbestos (Licensing) Regulations 1983.

Regulation 14 requires that any area in which work on asbestos is carried out be designated as: (1) an asbestos area, where the exposure of a person working for the whole of his working time is liable to exceed the action level; or (2) a respirator area, where the concentration of asbestos is liable to exceed any control limit.

General guidance on air monitoring is given in EH 42 *Monitoring Strategies for Toxic Substances* (HSE, 1989) and guidance for asbestos specifically is given in EH 10 *Asbestos: Exposure Limits and Measurement of Airborne Dust Concentrations* (HSE, 1990). EH 10 gives detailed information on the determination of action and control levels and on the monitoring and measurement of airborne asbestos, including accredited quality control laboratories, measurement methods, sampling and interpretation. It also contains a schedule dealing with sampling methods. Also relevant is *A Guide to Monitoring Airborne Asbestos in Buildings* (Keyes and Chesson, ACGIH 1989/33).

Further guidance on measurement is given in MDHS 39/3 *Asbestos Fibres in Air* (HSE, 1990).

Quality control laboratories are accredited for airborne asbestos measurement under the National Measurement Accreditation Scheme (NAMAS). This supersedes the earlier NATLAS scheme.

Where a process has the potential to generate asbestos dust, the methods of eliminating or reducing the generation of dust described in Section 25.5 should be exploited as is far as reasonably practicable.

Leaks from plant handling asbestos dust can cause serious contamination of the workplace atmosphere but are often invisible. They may be detected, however, using a dust lamp. This is illustrated in Figure 25.1 above, which shows the visualization of asbestos dust using a dust lamp.

An important part of the asbestos dust problem in the process industries relates to lagging. In many applications there are satisfactory substitutes and the industry has moved towards the use of these. Any use of asbestos should be confined to white asbestos. In practice, the use of asbestos is limited and it may not be easy to obtain.

Dust is particularly likely to be raised in removing lagging. The work should be segregated and workers should wear protective clothing and respiratory protective equipment. The area should be thoroughly cleaned after the work is complete.

Maintenance is particularly important in plant where asbestos dust may arise or in plant with asbestos lagging.

Where asbestos dust may be present, housekeeping measures assume particular importance. A high standard of cleanliness is necessary in the workplace. There need to be good facilities for washing and changing, and for cleaning protective clothing.

25.7 Ventilation

If an assessment of the air quality in the workplace shows it to be necessary, ventilation should be provided.

Accounts of ventilation are given in *Exhaust Hoods* (Dallavalle, 1952), *Plant and Process Ventilation* (Hemeon, 1963), *Fundamentals of Industrial Ventilation* (Baturin, 1972), *Basic Principles of Heating and Ventilation* (Bedford, 1974), *Air Conditioning and Ventilation of Buildings* (Croome-Gale and Roberts, 1975), *Handbook of Ventilation for Contaminant Control* (McDermott, 1976), *Advanced Design of Industrial Ventilation Systems for Contaminant Control* (Goodfellow, 1985) and by Grandidge (1969, 1977), Gill (1980b), Goldfield (1980), Caplan (1982), Cassells (1986–) and Fanger and Christensen (1986). The HSE guidance is given in

Principles of Local Exhaust Ventilation (HSE, 1975a), HS (G) 37 *An Introduction to Local Exhaust Ventilation* (HSE, 1987), EH 22 *Ventilation of the Workplace* (HSE, 1988) and HS (G) 54 *The Maintenance, Examination and Test of Local Exhaust Ventilation* (HSE, 1990). Further guidance is given in the BOHS *Air Contaminants Guide*, the *CIBSE Guide* by the Chartered Institute of Building Service Engineers (CIBSE)* (1977), *Ventilation Requirements* by the Building Research Establishment (BRE, 1981 Dig. 208), *Design of Industrial Ventilation Systems* (Alden and Kane, ACGIH 1982/6), *Heating, Ventilation and Air-Conditioning Analysis and Design* (McQuiston and Parker, ACGIH 1988/21), *Ventilation for Control of the Work Environment* (Burgess, Ellenbecker and Treitman, 1989 ACGIH/38), *Guide for Testing Ventilation Systems* (ACGIH 1991/58), *Industrial Ventilation: A Manual of Recommended Practice* (ACGIH 1991/67), *Industrial Ventilation Workbook* (Burton, 1991 AIHA/21), *Laboratory Ventilation Workbook* (Burton, 1991 AIHA/22), *Industrial Ventilation: Engineering Principles* (Heinsohn, 1991 ACGIH/66) and *IAQ and HVAC Workbook* (Burton, 1993 AIHA/25) and in the handbooks of the American Society of Heating, Refrigerating and Air conditioning Engineers (ASHRAE) (1990/4, 1991/5, 1992/6, 1993/7).

A relevant code of practice is BS 5925, which is particularly relevant to natural ventilation. The 1980 version was BS 5925: 1980 *Design of Buildings: Ventilation Principles and Designing for Natural Ventilation* which is that current for much of the ventilation literature quoted here. The current version is BS 5925: 1991 *Code of Practice: Ventilation Principles and Designing for Natural Ventilation*. The code for mechanical ventilation is BS 5720: 1979 *Code of Practice for Mechanical Ventilation and Air Conditioning in Buildings*.

The reasons for ventilation and ventilation rates for normal purposes are discussed in Chapter 10. Briefly, a degree of ventilation which maintains a suitable thermal environment commonly suffices for the other requirements also. BS 5925: 1980 recommends for factories a rate of 0.8 l/s per m^2 of floor area.

If there is airborne contamination, however, the situation is different. In this case the air requirement may depend primarily on the reduction of the contaminant concentration below the control limit.

As described in Section 25.3, the design should exploit to the extent practical methods of keeping the workplace atmosphere free of contamination which do not rely on ventilation.

If ventilation has to be used, there are two main methods available. These are general ventilation, which relies on dilution, and sometimes also on displacement, and local exhaust ventilation, in which contamination is removed close to its source so that the main workspace is not affected.

* The Chartered Institute of Building Services Engineers has twice changed its name in recent years, the previous acronyms being IHVE (Institution of Heating and Ventilation Engineers) and CIBS (Chartered Institute of Building Services). The guide referred to is also known as the *IHVE Guide* and the *CIBS Guide*.

25.7.1 Local exhaust ventilation

HSE guidance on local exhaust ventilation (LEV) is given in *Principles of Local Exhaust Ventilation* (HSE, 1975a), HS (G) 37 *An Introduction to Local Exhaust Ventilation* (HSE, 1987) and EH 22 *Ventilation of the Workplace* (HSE 1988). Further guidance is given in the BOHS *Air Contaminants Guide*.

LEV removes contaminants from the source directly into a ventilation system. It does not rely on the dilution or displacement effects of general ventilation. It should be designed to remove the contaminant from around the source rather than from around the operator.

An LEV system may be considered in terms of the following elements: (1) contaminant source, (2) hood, (3) ducting, (4) air filtration plant and (5) fan.

25.7.2 Contaminant source

The main problem in effecting LEV is the dispersion of the contaminant from the source. Once it has escaped from the immediate area of the source, it is very difficult to bring it under control. It is necessary, therefore, to obtain information on the behaviour of the contaminant leaving the source, such as its direction and velocity.

The air currents which influence the behaviour of the contaminant should also be studied. Air currents which are not essential to the process but are incidental or unconnected should be eliminated.

25.7.3 Enclosure and receptor hoods

It is usual to distinguish between two basic types of enclosure or hood systems used in LEV: (1) enclosures and receptor hoods and (2) captor hoods. Enclosures may be (1) total enclosures or (2) partial enclosures.

With a receptor hood the emission source is either inside or at the mouth of the hood. The hood receives contaminated air brought into it by air currents. These are either hot air currents rising from the process or cold air currents induced by the process. The air currents from a furnace and from a grinding wheel illustrate the two processes, respectively. The function of the fan in this type of system is simply to suck away the air entering the hood.

Total enclosure is the most effective arrangement, but it is not always practical. It is used in the chemical industry and for the handling of radioactive materials. It may involve remote operation using manipulators.

Where a total enclosure is used it needs to be air-tight so that it contains the vapour or dust handled, and strong enough to remain so. When such an enclosure is used, the space inside and the plant and equipment inside may be heavily contaminated. There is thus a need for measures to limit exposure when the enclosure has to be opened. These may include measures to remove the contaminant and measures such as procedures and/or interlocks to control access.

There are a number of types of partial enclosure, including (1) booths, (2) fume cupboards, (3) hoods over hot processes and (4) jet assisted hoods.

A partial enclosure should be no larger than is necessary for the purpose. The velocity of the air entering it should be high enough to overcome any tendency for the air inside to escape. Turbulence may be created within the enclosure by the working of equipment inside it and outside the enclosure by air currents.

For a partial enclosure the basic air flow required is given by

$$Q = AV \qquad [25.7.1]$$

where A is the area of the opening (m^2), Q is the volumetric air flow (m^3/s) and V is the inward superficial air velocity (m/s). The BOHS *Guide* states that whilst in quiet conditions an inward air velocity of 0.5 m/s may suffice, in more difficult circumstances 2 m/s or more may be needed, and that for normal situations in factories an air velocity of 1 m/s is often used. Depending on the nature of the enclosure, it may also be necessary to make an allowance for leakage at the joints of the enclosure. Guidance is given in the BOHS *Guide*.

A booth is a type of partial enclosure from which one side, or part of one side, is missing. It should be deep, since leakage due to eddies tends to occur round the edges of a shallow booth.

If the booth is large enough for an operator to work inside it, he should work at the front open face and not between the contaminant source and the air exhaust outlets.

A laboratory fume cupboard may be regarded as a special type of booth giving partial enclosure, but with a closure which can be closed to give almost total enclosure. There are many variations depending on the type of work to be done, but a fume cupboard usually takes the form of an open-fronted booth with a vertically sliding front window, or sash. The sash may be left open, partially closed or closed, and there are various arrangements designed to maintain a stable air flow and to ensure that air is drawn from both the top and bottom of the cupboard.

Relevant standards for fume cupboards are BS 7258: 1990 *Laboratory Fume Cupboards* and also BS DD 191: 1990 *Method for Determination of the Containment Value of a Laboratory Fume Cupboard*. Further guidance is given by D. Hughes (1980), Piney and Carroll (1983) and J.D. Cook and Hughes (1986).

Another receptor arrangement is a hood over a hot process. The design intent is that the hot gas rises from the process and flows into the hood. If the gas plume is not hot enough or if too much air is entrained into it, so that the total plume volume is too great and too cool, the hood may not operate as intended. The plume may miss the hood or may enter but may flow back out.

Methods are available for the design of such hoods. They include the plume models by Hemeon (1963) and Bender (1979) and methods of measuring plume volume and velocity, assisted by the use of cine or video film, developed by Bamford (1961) and Goodfellow and Bender (1980).

A further type of receptor arrangement is the jet-assisted, or push–pull, hood. This is used with an open surface such as a tank, where a jet of air is blown across the surface. The design intent may be frustrated if the jet is too powerful so that it carries the contaminant beyond the exhaust hood or if it strikes parts of the tank so that turbulence is created.

Models applicable to jet-assisted hoods of this type include those by Hemeon (1963) and Baturin (1972), whilst a practical application has been described by Huebener and Hughes (1985).

25.7.4 Captor hoods

The other main type of hood used in LEV is the captor hood. Whereas a receptor hood receives a flow of contaminated air carried into it, a captor hood draws the air flow in. The two types of hood may sometimes be similar in shape, but the principle of operation is different. A receptor hood operates on the push and a captor hood on the pull principle.

For a captor hood the air velocity required depends critically on the distance between the hood face and the contaminant source. For a normal shape such as a circle, square or rectangle (although not for a slot) the air velocity at a point only one hood face diameter from the centre of the hood face itself is typically only one-tenth of the face velocity. Thus a broad rule-of-thumb for a practical system is that the contaminant source should not be more than one hood face diameter from the hood face.

A more scientific approach is based on the concept of a capture velocity, which is the velocity induced at the source sufficient to capture the contaminant. Whilst there is no real design alternative to the use of capture velocity, the concept has limitations. It is most applicable where the contaminant at the source has a low velocity, but tends to break down where the contaminant is directed away from the hood at an appreciable velocity. The BOHS *Guide* states that, although capture velocities as low as 0.25 m/s are sometimes quoted, a value of 0.5 m/s should be taken as a practical minimum, and it uses in a subsequent illustrative example a velocity of 0.75 m/s.

A relation for the superficial velocity of air entering the hood has been given by B. Fletcher (1977). This is

$$\frac{V}{V_o} = \frac{1}{0.93 + 8.58\alpha^2} \qquad [25.7.2]$$

with

$$\alpha = \frac{X}{A^{\frac{1}{2}}}\left(\frac{W}{L}\right)^{-\beta} \qquad [25.7.3]$$

$$\beta = 0.2\left(\frac{X}{A}\right)^{-\frac{1}{3}} \qquad [25.7.4]$$

where A is the face area of the hood (m^2), L is the length of the hood (m), V is the capture velocity at distance X (m/s), V_o is the superficial velocity at the face of the hood (m/s), W is the width of the hood (m), X is the distance from the hood (m), and α and β are indices.

The performance of a captor hood may be enhanced by the use of flanges around the face inlet. The design of such flanges is treated in the BOHS *Guide*.

The volumetric flow of air required for a captor hood can be very much greater than for a receptor hood. The BOHS *Guide* gives a comparison of four systems. Of these four systems, the one most economical in air is a receptor hood with a small aperture in the face side, the second is a receptor hood with the whole face side missing, and the third is a captor hood with a large flange and the last a captor hood with no flange. The ratio of the volumetric air flow required by the last of these arrangements to that required by the first is 100:1.

25.7.5 Low volume high velocity system

A particular type of captor hood arrangement for LEV is the low volume, high velocity (LVHV) system. This system utilizes a small hood (typically $\leq 6\ cm^2$) placed very close to the contaminant source and a high capture velocity ($\approx$50–100 m/s). It may be used for vapour sources such as welding and for dust sources such as grinding. However, it is not easy to use and tends to be limited in application. Successful use requires that it be unobtrusive, correctly adjusted and properly maintained.

25.7.6 General ventilation

Local exhaust ventilation is the preferred method of ventilation, but there are circumstances in which it is not applicable, and in such cases resort may be made to general ventilation of the work space. However, such general ventilation is usually regarded as a comparatively ineffective method of contaminant control.

Some processes are operated outdoors, and it is often assumed that an outdoor location ensures negligible exposure. This is not necessarily so, and each case should be treated individually.

Indoors, there tend to be wide variations between the concentrations at different locations in the work space; the concentrations can differ by orders of magnitude. The enhancement of general ventilation may have little or no effect on the concentration at a particular point.

In general, the variability of the concentration of a contaminant at a fixed point outdoors tends to be very high. Indoors, the variability at a fixed point is much less.

General ventilation may have two effects. One is simply to reduce the concentration of contaminant by the introduction of more air. The other is to move the contaminant in a particular direction by displacement of air.

As described in Chapter 10, methods are available for the determination of the volumetric flow of air due to natural ventilation. Guidance is available in BS 5925: 1980. The BOHS *Guide* gives a worked example based on the BS 5925 method.

The concentration of contaminant resulting from general ventilation may be obtained on the assumption of perfect mixing in the work space, as described in Chapter 10. In practice, the concentration may be considerably higher. One approach to this problem is the method used by the ACGIH for the determination of concentration of a contaminant relative to the TLV. This method utilizes an empirical factor K which takes into account variations in the concentration with space and time, and allows for the toxicity of the contaminant. Values of K range from 3 to 10.

25.7.7 Air jets

Air jets are sometimes used as part of a system of general ventilation. They are of two types: those which draw air from within the work space and those which draw air from outside. In the first type the jet is used to promote mixing in the space. In the second type it may be used as a fresh air jet to provide a volume where the concentration of contaminant is low, but in this case it must be sufficiently near the point in question to effect this, otherwise the jet is liable to become contaminated with air from the work space.

The following equation is given by the CIBSE (1977) for the centre line velocity of a jet:

$$X = \frac{KQ}{V_x (A_f C_d)^{\frac{1}{2}}} \qquad [25.7.5]$$

where A_f is the free area of discharge (m^2), C_d is the coefficient of discharge, Q is the volumetric flow (m^3/s), V_x is the centre line velocity at distance X (m/s), X is the distance along the centre line (m) and K a constant. The value of C_d is taken as 1.0 for a well rounded nozzle and 0.6 for a sharp-edged orifice and that of K as 7.0 for a round nozzle and 5.7 for a standard grill, where the outlet velocity is 4–8 m/s.

The use of air jets can cause problems if the jet is not well integrated with the overall system design. Typical effects are undesired dispersion of the contaminant, interference with existing LEV systems, the creation of vortices where the contaminant becomes concentrated, and discomfort due to cold draught.

Use is also made of air curtains to provide a barrier to the flow of contaminant. The use of such a curtain can result in dispersion rather than containment of the contaminant and careful design is needed. Another device sometimes used is an air douche in which air is discharged at low velocity above the heads of workers.

25.7.8 Air replacement

The air removed by the ventilation system has to be replaced. It is usually recommended that this replacement air should enter through properly designed inlets. Air which simply leaks in through open doors, windows and cracks, may cause unpleasant draughts and may also set up air movements which affect the operation of an LEV system.

25.7.9 Design of ventilation systems

In designing a ventilation system for the control of a contaminant, this ultimate purpose needs to be borne constantly in mind. It is not uncommon for this objective to be lost sight of and for the design to degenerate into the mere provision of the mechanical elements of the system such as the hood, ductwork and fan. The BOHS *Guide* gives a series of quotations, starting with J.B.S. Haldane in 1907 and continuing into the 1980s. The following, from Hemeon (1963), though not the most recent, perhaps puts the problem most clearly:

> It sometimes seems that engineers experience such sheer satisfaction in their ability to handle the design of duct work on a neatly quantitative basis, that they are led to slight the initial problem of selecting suitable exhaust or ventilation rates as though they were a minor detail to be covered as quickly as possible… whereas the part they slight is the essential of industrial ventilation.

For this reason the guide advocates design leadership by an occupational hygienist.

Accounts of the mechanical design of ventilation systems are given in the texts quoted. In particular, *Local Exhaust Ventilation*, the *BOHS Guide* and the *IChemE Dust Control Guide* give detailed treatments, dealing with overall system design, ductwork, fittings, multi-branched systems, fans, and air cleaning and disposal.

Guidance on the commissioning of ventilation systems is given in *Principles of Local Exhaust Ventilation*, BS 5720, the *Commissioning Code* of CIBSE (CIBS, 1977; CIBSE, 1978–), and the BOHS *Guide*.

Where the system is a multi-branched one, the balancing of the flows is of particular importance.

25.7.10 Maintenance of ventilation systems

It is important that any ventilation system for the control of contaminants be properly examined and maintained. HSE guidance is given in HS(G) 54 *The Maintenance, Examination and Test of Local Exhaust Ventilation* (HSE, 1990).

Inspections have found that the effectiveness of many industrial ventilation systems is low. Sometimes this is due to inefficient functioning of the mechanical items due to poor maintenance. But it is also possible for these items to be working as intended but for the ventilation achieved to be ineffective. This may arise, for example, if the contaminant source has been moved somewhat further from the hood.

The prominence given in regulations to maintaining the whole system so that it operates as intended reflects the problem. As described earlier, Regulation 9 of the COSHH Regulations requires that for LEV plant the maximum interval for thorough examination and test is 14 months, or as given in Schedule 3 to that regulation. The CLAW Regulations and the CAWR also contain requirements for LEV system maintenance.

Checklists for the maintenance of LEV systems are given HS(G) 54 and the BOHS *Guide*.

25.8 Skin Disease

Thus far the discussion has dealt with toxic substances which are airborne. It is also necessary to prevent corrosive and toxic chemicals from causing irritation of the skin leading to skin disease, or dermatitis, and from entering the body through the skin.

Guidance on skin disease is given in MS 3 *Skin Tests in Dermatitis and Occupational Chest Disease* (HSE, 1977), EH 26 *Occupational Skin Diseases* (HSE, 1981) and MS 24 *Health Surveillance of Occupational Skin Disease* (HSE, 1991). Further accounts of skin disease are given in *Occupational Diseases of the Skin* (L. Schwartz, Tulipan and Birmingham, 1957) and *Manual of Contact Dermatoses* (Fregert, 1974) and by McCreaney (1969, 1977), Rycroft (1979, 1980, 1980 LPB 58) and Gadian (1983). Aspects of skin disease in the petroleum industry are dealt with in *Petroleum Hydrocarbons: their Absorption Through and Effect on the Skin* (CONCAWE, 1984 84/54) and *Factors Affecting the Skin Penetration and Carcinogenic Potency of Petroleum Products Containing Polycyclic Aromatic Compounds* (CONCAWE, 1990 90/55).

Occupational skin disease is the most common cause of disablement in industry. Statistics are given in the *Health and Safety Statistics 1990–91* (HSE, 1992b). There are a number of different ways of arriving at a figure for such disease, but the number of new cases is of the order of 40 000 per year.

The types of chemical which cause skin disease are classified as (1) contact irritants, (2) contact sensitizers and (3) photosensitizers. Contact irritants cause direct damage to the skin. Contact sensitizers cause a specific allergic response to develop over a period. Photosensitizers may be either irritants or sensitizers, but require the additional stimulus of sunlight or ultraviolet light.

Substances which are liable to cause skin disease are chemicals, cutting oils, degreasing agents, tar and pitch. It may also be caused by physical agents such as heat, cold, humidity, light and ionizing radiations.

Prevention of skin disease should be based on engineering measures to eliminate the causal agent, supplemented where necessary by personal protection. Where chemicals have to be handled, it is essential to use the proper methods and to wear the appropriate protective clothing, to observe the highest standards of personal hygiene, to change working clothes, including underwear, frequently and to take a thorough shower each day. Any break in the skin should be covered. Skin rashes should be reported, and wounds treated, promptly.

25.9 Physico-chemical Hazards

There are a number of physico-chemical effects which are very simple and familiar to the engineer, but which have implications often not fully appreciated, particularly by process and maintenance personnel.

An account of some of these effects has been given by Jennings (1974a,b). They include:

(1) density differences –
  (a) gases and vapours,
  (b) liquids;
(2) phase changes;
(3) vapour pressure;
(4) flashing liquids;
(5) nearly immiscible liquids;
(6) heat of mixing;
(7) exothermic reactions;
(8) impurities.

At constant pressure the density of a gas or vapour ρ_g is proportional to the molecular weight M and inversely proportional to the absolute temperature T

$$\rho_g \propto \frac{M}{T} \qquad [25.9.1]$$

Density differences can cause the gas or vapour to flow in unexpected ways.

In one case, a manhole in a reboiler containing benzene was left open, some benzene vapour escaped and poured down so quickly into the base of the room that the operator was killed before he could put on a respirator.

Another incident involved a hydrogenation vessel which was shut down for repair, but into which hydrogen continued to leak through a valve that was only partially closed. When the top manhole cover was taken off to admit a charge of carbon dioxide as an inert blanket, there was a flash of fire. Since the hydrogen was much less dense, enough air had presumably entered to form a flammable mixture.

Differences in liquid density can give rise to very high pressure in equipment and to layering. In one incident the discharge and suction valves were shut on a pump full of ethylene glycol and the pump was left running. The liquid heated up and the volumetric expansion of the

liquid generated a pressure sufficient to crack the pump casing.

The effect of layering due to the difference of densities of two liquids is illustrated by the following case. A mixture of liquid caustic soda and phenol was being prepared in a reaction vessel by an operator. The addition was made without agitation and the phenol formed a separate layer on top of the caustic soda. When the agitator was switched on, there was a violent reaction and about half the charge was ejected through the top opening, which had a hinged lid, onto the operator.

The volume changes associated with a change of phase, particularly changes between liquid and vapour, can produce violent effects. At atmospheric pressure, for example, one volume of liquid water vaporizes to give about 1600 volumes of steam.

A road tanker was being filled with hot tar at a temperature just below 100°C when the pump failed. In accordance with normal practice the tar line was blown out with steam. Since the tank was only half full, the driver went on to another site to top up and so obtain a full load. Here the tar was at a temperature in excess of 100°C and a few seconds after the filling began hot tar was ejected from the manhole. The cause was vaporization of the steam condensate left in the tank from the steam blowing operation at the first site.

Conversely, sudden contraction of vapour can create a vacuum and cause a vessel to implode or to draw in air. An important particular case is the situation which occurs when heat input is lost on the reboiler of a distillation column. Rapid condensation of the vapour in the column may create a vacuum which draws air in through the vent and may thus cause an explosive mixture to form. This may be prevented by the use of nitrogen injection.

Powerful effects are also produced by the variation of the vapour pressure with temperature. For a pure liquid the relation between the vapour pressure and temperature may be represented by the Antoine equation

$$p^{o} = \exp\left(A - \frac{B}{T + C}\right) \qquad [25.9.2]$$

where p^{o} is the vapour pressure, T is the absolute temperature, and A, B and C are constants. For most liquids the vapour pressure doubles over a temperature range of about 8°C.

For ideal liquid mixtures Raoult's law applies

$$p_i = p_i^{o} x_i \qquad [25.9.3]$$

where p_i^{o} is the vapour pressure of the pure component i, p_i is the partial pressure of component i and x_i is the concentration of component i (mole fraction).

But, if instead the liquids are immiscible, then for each liquid

$$p_i = p_i^{o} \qquad [25.9.4]$$

In both cases the total pressure P is given by Dalton's law

$$P = \Sigma p_i \qquad [25.9.5]$$

In the general case some of the components may be inert gases.

The effect of vapour pressure is illustrated by a case in a works producing chlorine by the mercury cell process where a worker was found to have persistently high mercury in his urine, even though he hardly ever went into the cellroom. His main work was the removal of ebonite lining from mild steel sections used in the cellroom equipment. The work involved the application of heat. This heat was sufficient to cause traces of mercury lodged in cracks in the ebonite to exert an appreciable vapour pressure.

A common phenomenon associated with vapour pressure is cavitation in pumps. This occurs if the suction pressure is low and the liquid temperature is high. Pockets of vapour form and collapse as the local pressure falls below or rises above the vapour pressure. The resultant erosion and pitting is extremely damaging to the pump.

A Dowtherm furnace started up and the pressure rose suddenly from 15 to 110 psi. Water had entered the system and both liquids were exerting their full vapour pressure. In this instance the pressure relief valve operated and prevented an accident.

If a liquid at a given pressure is let down to a lower pressure such that the boiling point at the lower pressure is less than the original temperature of the liquid, liquid immediately flashes off until the lower pressure boiling point is reached, the amount of vapour formed being determined by the heat balance.

A tank had been cleaned by boiling water in it under pressure. The operator opened a vent to release the pressure, but loosened a manhole before the venting was complete. Large amounts of boiling water and steam issued out around the cover.

Liquid systems in which there are two separate liquid phases are loosely referred to as 'immiscible', although there is always some mutual solubility, so that 'nearly immiscible' would be a more accurate description. Consider a system with two nearly immiscible components A and B. At equilibrium the phase which is nearly all A is saturated with a small quantity of B. If this phase has separated out, both A and B exert their full vapour pressure. If B has a high vapour pressure, a considerable proportion may be evolved.

An operator drained water from a tank in which there was a water layer covered with a benzene layer. The benzene in the water exerted an appreciable vapour pressure and the operator suffered benzene poisoning.

When two liquid chemicals are mixed together, there is a heat of mixing. Whilst this is zero for an ideal mixture and low for many mixtures, for others it is appreciable.

Owing to a failure of communication a tanker of hydrochloric acid was unloaded into a storage tank used for sulphuric acid. When about half of the 3000 gal load had been transferred, there was a violent explosion, which raised the tank several inches off the ground and buckled it, and broke the inlet and outlet lines.

In another case a violent explosion occurred when mixing took place between very strong caustic soda, which was lying on the bottom of a vessel and was covered by a solid crust, and weak caustic soda above it.

Reaction kinetic effects, especially in exothermic reactions, are discussed in Chapter 11.

A particular case of importance is situations in which there is inadequate agitation in a chemical reactor. The reactants are allowed to build up without agitation and

then react explosively, either spontaneously or when agitation is started.

One incident involved a sulphonation process in which benzene and concentrated sulphuric acid were premixed before transfer to a reaction vessel. On one occasion the agitator was not used and the reactants were transferred unmixed. The operator noticed this and quickly switched on the reactor agitator. There was a rapid reaction, benzene vapour was evolved, a flammable mixture was formed in the room and it ignited.

Impurities can cause violent reactions or severe corrosion.

An operator was transferring thionyl chloride by vacuum from a 55 gal drum through a stainless steel hose when the hose developed a leak. He obtained another hose, checked that nothing drained from it and substituted it for the first. When he opened the feed valve, the hose ruptured. The accident was caused by a small amount of water which was left in the hose and which reacted violently with the thionyl chloride, releasing large volumes of hydrogen chloride and sulphur dioxide. Calculation showed that one teaspoonful of water would be enough to generate a pressure of 2800 psig in the hose.

Corrosion not only reduces the strength of equipment but also generates gases.

An apprentice under training was erecting some pipework. He required a blank flange of a particular size and noticed one on some redundant pipework nearby. When he attempted to remove the blank, acid sprayed in his face. The pipework had been used previously for concentrated sulphuric acid and corrosion had generated hydrogen, which pressurized the pipe.

25.10 Ionizing Radiation Hazards

Materials and machines which give off ionizing radiation are widely used in industry. They are potentially very hazardous, but they may be handled safely by taking proper precautions.

The legislation covering the use of ionizing radiations is discussed in Chapter 3. That of principal relevance here is the Ionizing Radiations Regulations 1985. The associated ACOP is COP 16 *The Protection of Persons against Ionising Radiation arising from any Work Activity* (HSE, 1985).

Engineering aspects of ionizing radiations are described in *Radioactivity for Engineers* (Coombe, 1968) and health and safety aspects are described in *Radiation Hygiene Handbook* (Blatz, 1959), *Radiation Protection Standards* (L.S. Taylor, 1971), *Principles of Radiation Shielding* (Chilton, Shultis and Faw, 1984), *Industrial Radiation Hazards Deskbook* (Cheremisinoff, Cheremisinoff and Teresinski, 1987 ACGIH/12) and *Radiation Protection* (Shapiro, ACGIH 1990/48) and by H.H. Fawcett (1965c), Bennellick (1969, 1977), Brodsky (1978–), Doran (1980), Harrington (1980b), Dennis (1982) and Kielman and Fawcett (1982).

A code relevant to potential exposure to radioactive materials during a fire is NFPA 801: 1991 *Facilities Handling Radioactive Materials.*

The hazard from sealed sources, from machines designed to generate ionizing radiations such as X-rays and from machines which give off radiations adventitiously is one of external exposure, but unsealed sources present the further hazard of internal exposure arising from ingestion.

Ionizing radiations are a complex and specialist matter and only a very limited treatment is given here. A more detailed treatment of types and units of radiation is given in Appendix 20. COP 16 gives detailed coverage of a large number of industrial aspects.

25.10.1 Types and units of radiation

There are three main types of radioactive particle or ray: (1) α-particles, (2) β-rays and (3) γ- and X-rays. α-particles have a relatively large mass and short range, being stopped by an air gap of about 8 cm or a sheet of paper, and generally they present little external radiation hazard, but are dangerous if they get inside the body. β-rays (or particles) have a much smaller mass and greater penetrating power. Their range in air is about 10 m, but they are usually stopped by a few millimetres of solid material. γ-rays and X-rays are electromagnetic radiations which have a range of a few hundred metres, but can be stopped by a few millimetres of lead or by 0.5–1 m of concrete.

In the SI system the units of radiation are: for activity, the becquerel (By); for absorbed dose the gray (Gy); and for the dose equivalent, the sievert (Sv). The dose equivalent is the product of the absorbed dose and a quality factor (QF). The corresponding units in the older system are the curie (Ci), rad (rad) and rem (rem), respectively.

25.10.2 Effects of exposure

α-Particles destroy bone marrow so that the red corpuscles are not replaced. β-rays give rise to skin burns, skin cancer, dermatitis and eye disease. γ-rays and X-rays cause skin burns and cancer and ageing effects. Fairly severe exposure is required to cause sterility, but genetic effects are believed to be proportional to exposure.

25.10.3 Industrial applications

Industrial applications of ionizing radiations include the following:

(1) radioactive process materials;
(2) Radioactive auxiliary materials –
  (a) tracers,
  (b) sorting aids,
  (c) quality control aids,
  (d) static eliminators,
  (e) instruments;
(3) γ- and X-rays –
  (a) non-destructive testing,
  (b) quality control;
(4) irradiation –
  (a) food preservation,
  (b) cold sterilization,
  (c) polymerization.

Some process materials, such as radioactive metals, are themselves radioactive.

Radioactive materials are commonly used as tracers. Examples are the use of ^{24}Na, ^{59}Fe and ^{60}Co in work on mixing, piston ring wear and refractory wear, respectively, and of various tracers in following the progress of

pigs or of interfaces between products in pipelines and in detecting leaks in water and other pipe systems.

Items on which sorting or quality control is to be carried out may be tagged with a radioactive material. Radioactive sources are used to ionize the air and so dissipate static electricity. Instruments which use radioactivity include level measuring instruments that measure the height of the liquid surface and ionization chambers which detect the presence of smoke.

γ-ray sources are used to detect flaws in castings. The castings are grouped around the source with photographic plates behind them. Similarly, the non-destructive testing of pressure vessels and components, and particularly welds, is carried out using X-rays. The latter are also used in X-ray fluoroscopy for the inspection of items on conveyor belts for quality control purposes.

Applications of irradiation in polymerization include the vulcanization of rubber and polymerization of high melting point polyethylene.

25.10.4 Measurement of radiation

Measurements of radiation are made both on the plant and on the personnel. In the first case the objective is to check radiation flux levels and releases, in the second to monitor exposure.

Portable devices for measuring the exposure of personnel include film badges and pocket ionization chambers. Both types measure β-, γ- and X-rays.

Radiation on the plant or from contamination is measured by instruments such as Geiger–Muller counters and scintillation counters. Except for scintillation counters these instruments do not measure α-particles, but special α-measuring instruments are available.

25.10.5 Limits for exposure

Occupational exposure to radiation should always be kept as low as practicable. The established limits should be observed, but since any level of radiation may involve some risk, every effort should be used to minimize exposure.

Recommendations on limits for exposure are made by the International Commission on Radiological Protection (ICRP). These recommendations are widely applied internationally.

In the UK the National Radiological Protection Board (NRPB) makes recommendations to government on working limits, taking into account the ICRP recommendations.

The statutory limits for ionizing radiations are given in the Ionizing Radiations Regulations 1985 and are:

Adult workers: dose limit	50 mSv in any calendar year
Adult employees: investigation level	15 mSv in any calendar year
Members of public: dose limit	5 mSv in any calendar year
Members of public exposed over long periods: dose limit	1 mSv annual average

The following are the limits now recommended by the NRPB (1993):

Adult workers: dose limit	20 mSv in any calendar year
Adult employees: investigation level	15 mSv in any calendar year
Students and apprentices	6 mSv in any calendar year
Members of public: dose limit	1 mSv in any calendar year

0.3 mSv from any single source

25.10.6 Control of exposure

As in industrial hygiene generally, control of radiation exposure depends on deciding acceptable limits of exposure, designing the plant to minimize release, operating systems which minimize exposure and monitoring the personnel exposed.

Radiation may be contained within the equipment by shielding. This may take the form of lead a few millimetres thick. Protection of equipment giving off radiations may be provided by interlocks.

If some exposure is unavoidable, measures should be taken to minimize it. Since the dose is inversely proportional to the square of the distance and proportional to time, the distance from the radiation source should be as great and the time of exposure as short as possible.

Contamination from unsealed sources requires special measures for control and decontamination. These are discussed by Bennellick (1969, 1977).

All personnel who may be exposed to radiation should be monitored. Principal methods of monitoring include the carrying of personal radiation meters and the testing of blood. If tests indicate that a person is nearing the limit of exposure, he should be withdrawn temporarily or permanently from the work.

25.11 Non-Ionizing Radiation Hazards

Ionizing radiation is not the only kind of radiation which may be hazardous. There are a number types of non-ionizing radiation which can have harmful effects.

Accounts of non-ionizing radiation are given by Harrington (1980b), Kanagasbay (1980), Kielman and Fawcett (1982), McKinlay (1982) and Pilborough (1989). Guidance is available in the series *Nonionizing Radiation Guides* (AIHA, 1977–/3).

25.11.1 Electromagnetic spectrum

The electromagnetic spectrum is divided by wavelength into the following regions:

Cosmic rays	$< 10^{-4}$ nm
γ-rays and X-rays	10^{-4}–10 nm
Ultraviolet	10–400 nm
Visible region	400–700 nm
Infrared	700 nm–1 mm
Microwaves	1 mm–1 m
Radio waves	>1 m

The boundaries have developed by usage and are adopted by convention. Non-ionizing radiation is conventionally taken as that radiation which has a wavelength exceeding 100 nm, and thus starts within the ultraviolet region.

25.11.2 Artificial sources

Artificial sources of non-ionizing radiation include: in the ultraviolet (UV) region, welding; in the infrared (IR) region, welding, furnaces and lasers; in the microwave and radiofrequency (RF) regions, microwave ovens, communications equipment and radar.

25.11.3 Health effects

The health effects of exposure to non-ionizing radiation are felt mainly on the eyes and skin. UV, IR, and microwave and RF radiations can each cause damage to both these parts of the body.

Thermal injury occurs when the rise in the temperature of the tissue is more than a few degrees. Thermomechanical damage ensues when thermal expansion of tissue is at such a rate that it results in explosive disruption. Photochemical injury is caused by absorption of a greater dose of energy than the body's repair mechanism can handle.

25.11.4 Ultraviolet radiation

UV radiation is most harmful in the waveband 200 to 315 nm. Acute injury depends essentially on the total dose, whether this be received with a few seconds or over some hours.

The effect of overexposure on the eye is exemplified by such conditions as 'welder's flash' and 'snow blindness' the condition is known as photokeratitis and is painful but generally reversible. The acute effect on the skin is erythma, or sunburn. Long-term overexposure of the skin leads to the chronic condition of skin cancer.

Guidance on UV radiation is given in *Ultraviolet Radiation* (AIHA, 1991/14a).

25.11.5 Infrared radiation

Visible and IR radiation entering the eye is focused on the retina and can cause damage, but this is usually averted. The reaction to a bright light is to avert the eye and this aversion response, occurring typically with 0.25 seconds, usually ensures that damage is avoided.

The main cause of injury to the skin from IR is thermal damage. A particularly hazardous form of IR radiation is that from a laser.

25.11.6 Laser radiation

A laser produces an intense monochromatic beam of non-ionizing radiation, either as continuous wave (CW), a single pulse or a series of pulses. The beam from some lasers can cause damage, particularly to the eye.

Guidance on lasers is given in PM 19 *Use of Lasers for Display Purposes* (HSE, 1980) and *Safety in Universities—Notes of Guidance, Part 2:1 Lasers* by the Committee of Vice-Chancellors and Principals (CVCP) (1992). A relevant code is BS EN 60825: 1992 *Radiation Safety of Laser Products, Equipment Classification and Users Guide.* Further guidance is given in *A Guide for the Control of Laser Hazards* by the ACGIH (1990/41).

Laser products are classified according to the maximum permissible exposure (MPE) of the eyes and skin, and to the associated accessible emission level (AEL).

Class 1 laser products are those which are inherently safe. Class 2 laser products are not inherently safe but have a power so limited that eye damage should not result over a duration of 0.25 seconds for a blink reflex. Classes 3A, 3B and 4 cover higher power products.

A laser may or may not produce a beam in the visible part of the electromagnetic spectrum, so that a person working with one which does not may be unaware that he has been exposed.

Personnel working with laser equipment should wear safety glasses appropriate to the class of laser concerned. A high level of ambient lighting is beneficial in that it restricts pupil size.

Since different classes of laser have very different power outputs, arrangements satisfactory for one class may not be so for a higher power class.

The use of lasers requires a safe system of work, the principal elements of which are control of access, warning notices and lights, and, possibly, interlocks.

Work with lasers should be subject to health surveillance.

25.11.7 Protection and control

The principles of protection from non-ionizing radiations have many similarities with those for protection against the hazards already considered. The first line of defence is engineering measures to eliminate or reduce exposure, the second is systems of work for the control of exposure and the third is personal protective equipment.

25.12 Machinery Hazards

Accidents caused by moving machinery have always been a serious problem in industry. The reduction of this type of accident has been one of the main concerns of industrial safety legislation. The development of this legislation has been described in Chapter 3.

Guidance on the hazards and safe use of machinery is given in two series of publications by the HSE, the HSW series (*Health and Safety at Work Booklets*) and the PM (Plant and Machinery) series. The former include HSW 3 *Safety Devices for Hand and Foot Operated Presses* (HSE, 1971) and HSW 41 *Safety in the Use of Woodworking Machines* (HSE, 1970). The PM series includes PM 1 *Guarding of Portable Pipe-threading Machines* (HSE, 1984), PM 21 *Safety in the Use of Woodworking Machines* (HSE, 1981), PM 22 *Training Advice on the Mounting of Abrasive Wheels* (HSE, 1983), PM 23 *Photo-electric Safety Systems* (HSE, 1981), PM 41 *Application of Photo-electric Safety Systems to Machinery* (HSE, 1984) and PM 65 *Worker Protection at Crocodile (Alligator) Shears* (HSE, 1986). A relevant standard is BS 5304: 1988 *Code of Practice of Safety of Machinery.* Accounts of safe working with machinery are given by Haigh (1969, 1977) and Bramley-Harker (1969, 1977).

25.12.1 Machine guarding

The law on the safeguarding of machinery has become progressively stricter. Requirements are given in the Factories Act 1961, Sections 12–15. These sections state that prime movers and their flywheels should be securely fenced, as should electric motors and generators, transmission machinery and other dangerous machinery unless safe by construction or position, that devices for promptly cutting off the power from transmission machinery should be provided in every place where work is carried out, that efficient mechanical appliances should be provided to move driving belts to and from fast and loose pulleys and that driving belts should not

rest or ride on revolving shafts when the belts are not in use.

Secure fixed fencing is the preferred method of guarding machinery. The fencing should be strong so that it fulfils its protective function and does not deteriorate as a result of frequent removal and replacement for maintenance. It should be secure and removable only by the use of tools.

The fencing should enclose the parts guarded completely. Many accidents occur on equipment where the fencing is incomplete and where a worker is liable to catch his hand between the moving part and the guard.

In some applications, however, complete enclosure by fencing is not possible, because it is necessary to feed material or components into the machine. In such cases partial fencing may be used. The space left unprotected should be big enough to allow the required access for materials but should exclude the hand. Thus complete fencing is normal for machinery such as revolving shafts, belt drives and gear wheels, but partial fencing is used on power presses and calenders.

Partial fencing may be complemented by distance fencing, which prevents the operator approaching too close to the machine.

If a fixed guard is not practical by reason of the nature of the operation, a permissible alternative for machinery other than prime movers or transmission machinery is a device which automatically prevents the operator from coming in contact with the dangerous plant.

Some other methods of providing protection on these lines are (1) feeders, (2) interlocks and (3) trips.

A feeder device such as a side, chute or roller is used to allow material or components to be fed into a machine without the necessity for a worker to put his hand in.

It is often necessary to have access to machinery for purposes such as maintenance. In this case use may be made of an interlock which prevents access until the machine is stopped and prevents start-up while it is unguarded.

The stopping of the machine requires a braking system. The interlock should ensure that the machine has been completely stopped before access is possible.

With some machinery fencing is not a practical solution. An alternative approach is the use of a trip. Trip devices include safety bars, photoelectric cells and proximity switches. Again a braking system is necessary to ensure that the machine stops quickly.

It is essential for there to be good maintenance both of the machine itself and of the fencing and other protective systems such as interlocks, trips and brakes.

Operators should be trained in the use of the machinery itself and in the protective systems. Likewise, maintenance personnel should have training in the maintenance of both machine and protective system. In some cases this training is the subject of a specific statutory requirement. The Power Presses Regulations 1965, for example, specify the training required for the maintenance of such presses.

25.12.2 Running nips

A large proportion of the hazards on moving machinery arises from running nips. A running nip occurs when material runs onto or over a rotating cylinder. Running nips exist, for example, where a belt runs over a pulley wheel, a chain over a sprocket wheel, a conveyor over a roller or material over a drum, or where two rolls create an in-running nip. Running nips cause many accidents and the accidents are frequently serious.

An account of running nips is given by S.F. Smith (1969, 1977). One relevant code is BS 5667: 1979– *Specification for Continuous Mechanical Handling Equipment: Safety Requirements*, particularly Part 18 *Belt Conveyors—Examples of Guarding Nip Points* and Part 19: 1979 *Conveyors and Elevators with Chain Elements—Examples of Guarding Nip Points*. Another code is BS 7300: 1990 *Code of Practice for Safeguarding of the Hazard Points on Troughed Belt Conveyors*.

Typically accidents arise because an operator gets his clothing caught in a nip or slips and falls into one, because he tries to make some adjustment to the material running onto a cylinder or to remove foreign bodies or to clean rollers, or because the machinery is started up by mistake. Where material runs onto a roller, it is safer if it runs over the top so that the hazard is confined to the sides of the nip.

Most of the methods of protection described for machinery in general are applicable to running nips. The preferred method is complete fixed fencing, but partial fencing, distance fencing, feeders, interlocks and trips are also used. Again if interlocks or trips are used, it is essential that braking be such that it can stop the machinery sufficiently quickly. Often several measures are used in combination. Protection on a conveyor belt, for example, may use a combination of fixed fencing, distance fencing, interlocks and trip wires.

25.12.3 Inadvertent starts

Some accidents occur due to the inadvertent starting of machinery. A study of this type of accident has been made by Rouhiainen (1982), who investigated some 105 incidents involving inadvertent starting of machinery in a range of industries. Of the six incidents in the chemical industry, four involved presses and two involved guillotine shears, machinery not particularly characteristic of the industry. On the other hand, there were 14 accidents with conveyors, 8 with other transferring and lifting machines, and 3 with packaging machines.

The primary causes assigned included 24 intentional starts, 26 starts caused by human error, 21 starts caused by accidentally touching the start button, and 16 starts caused by the machine itself.

The author proposes measures to prevent inadvertent starts in both maintenance and normal operations. The former include the disconnection of sources of electrical and mechanical energy, such as would be applied in a good permit-to-work system. The latter include the use of barriers, interlocks and touch stopping devices.

The protective measures described in the guidance in Section 25.12.1 include protection against inadvertent starts.

25.12.4 Abrasive wheels

Accidents with abrasive wheels used for grinding are usually due to wheel failure. The number of accidents is small, but this is so only because great care is usually taken with grinding operations.

Relevant statutory requirements include the Grinding of Metals (Miscellaneous Provisions) Regulations 1925. Guidance is given in PM 22 *Training Advice on the Mounting of Abrasive Wheels* (HSE, 1983) and HS(G) 17

Safety in the Use of Abrasive Wheels (HSE, 1984). Accounts of abrasive wheels is given by Blackshield (1969) and Southwell (1977).

The main cause of wheel breakage is accidents, including damage to the wheel by mechanical shock and unchecked traverse of the work onto the side of the wheel.

Excessive rotational velocity is also dangerous. For a given wheel a velocity is specified and should be adhered to. The velocity depends on the type of grinding. In high velocity grinding the velocity is about twice that for normal grinding. It is essential to avoid using wheels made for normal velocity in high velocity work.

Other causes of breakage include excessive heating and excessive work pressure.

Safety measures in grinding work include selection and care of the wheels, proper mounting of the wheels, running at the specified speed and eye protection for the operator.

25.13 Electricity Hazards

Accidents in factories due to electricity are frequently associated with a failure to isolate or earth electrical equipment or to temporary or defective equipment.

The use of electrical equipment in factories is governed by the Electricity at Work Regulations 1989, which supersede the Electricity (Factories Act) Special Regulations 1908 and 1944. Guidance is given in HS(R) 25 *Memorandum of Guidance on the Electricity at Work Regulations 1989* (HSE, 1989). A further treatment is given in *Handbook on the Electricity at Work Regulations* (Marks, 1991).

HSE guidance on electrical safety is given in HS(G) 13 *Electrical Testing: Safety in Electrical Testing* (HSE, 1980), GS 27 *Protection Against Electrical Shock* (HSE, 1984), GS 37 *Flexible Leads, Plugs and Sockets* (HSE, 1985), PM 64 *Electrical Safety in Arc Welding* (HSE, 1986), PM 32 *Safe Use of Portable Electrical Apparatus (Electrical Safety)* (HSE, 1990) and GS 47 *Safety of Electrical Distribution Systems in Factories* (HSE, 1991). Further accounts are given in *Electrical Safety Engineering* (Fordham Cooper, 1986) and by Haigh (1969, 1977), Crom (1977) and Eales (1977a–c).

Some British Standards on electricity and electrical work are given in Appendix 27. One of particular relevance here is BS 2769: 1984 *Hand-held Electric Motor-operated Tools*. Part 1 of this standard gives general requirements for all types of tool and Part 2, Sections 0–14, describe requirements for some 14 types of tool.

Electrical equipment should be installed, inspected, tested and maintained only by competent electricians.

Equipment should be regularly inspected and serviced. Equipment on which repair is to be done should be disconnected from the supply until the work is complete. The importance of this instruction should be made clear to both electrical and other maintenance personnel. Defective equipment should be taken out of use and completely disconnected from the supply until it is repaired.

Temporary wiring should be avoided as far as possible, but if used should be to a safe standard and properly earthed. It should be regularly inspected and repaired as necessary and it should be replaced by a permanent installation as soon as possible.

Circuits should not be overloaded, as this increases the risk of fire. Loading should be carefully supervised and circuits protected by fuses or circuit-breakers.

Leads should have wires of the standard colours, which in the UK are brown for live, blue for neutral and green and yellow for earth. Leads of other colours on old or imported equipment should preferably be replaced.

A large proportion of electrical accidents involves portable tools. As described in BS 2769: 1984, the types of portable tool are (1) earthed tools and (2) all-insulated or double-insulated tools. It is essential to ensure that an earthed tool is not used unless it is properly earthed. All portable tools should be maintained and tested regularly.

Cables and plugs are vulnerable and require attention. Wear occurs particularly at the points where the cable enters the tool or plug. Cable grips reduce this problem. Flexible cables should be positioned so that they are not damaged by heavy equipment.

Tools with low voltage (110 V or, in damp conditions, 50 V) should be used wherever practicable. The plug/socket system for such tools should be such as to prevent their being plugged into the normal mains.

25.14 Other Activities and Hazards

The hazards associated with certain common activities are considered in this section. Other activities and hazards are treated in other chapters. Those associated particularly with maintenance, for example, are covered in Chapter 21.

25.14.1 Lifting and carrying

Handling, lifting and carrying activities are discussed in HSW 1 *Lifting and Carrying* (HSE, n.d.), *Work Practices Guide for Manual Lifting* (NIOSH, 1981 Publ. 81–122) and *Manual Material Handling* (Kroemer, McGlothlin and Bobick, 1989 AIHA/16) and by Halliday (1969, 1977), A.R. Hale (1984) and Kroemer (1992).

The Factories Act 1961 states that 'a person shall not be employed to lift, carry or move any load so heavy as to cause injury'.

According to the *Health and Safety Statistics 1990/91* (HSE, 1992b), accidents involving the handling, lifting and carrying of goods were responsible for some 55 477 injuries, including 2 fatalities and 1257 non-fatal major injuries reported to the HSE. In many cases such accidents result in permanent injury, such as back trouble or hernia, and in long periods of absence from work.

These activities are often treated in terms of sudden injury arising from a single incident. But in fact much injury occurs due to cumulative strain caused by incorrect practices over a long period.

The first essential is that the ergonomics of the handling task should be right. This means not only that the weight to be handled should not be excessive, but also that the adoption of awkward positions should not be necessary and that suitable aids such as handles, platforms, rollers, etc., should be provided and sufficient time should be allowed.

Then it is necessary that workers doing handling work observe some basic principles relating to grip, the position of the arms, chin and feet, back posture and the use of body weight. The grip should be a full palm rather than a fingertip grip. The arms should be held close to the body and fully extended so that the weight is taken by the body itself rather than the arms. The chin should be kept in, which reduces the risk of spinal injury. The back should be kept flat. This prevents compression of the abdominal contents, which leads to hernia, and in conjunction with correct foot positioning gives better mechanical advantage. The feet should be positioned slightly apart to give good balance. The weight of the body should be used ballistically, avoiding jerky actions. The use of body weight is one of the principles underlying judo and allows large weights to be moved with minimum effort.

There are wrong and right ways of lifting a heavy object. If the object is lifted with the back curved, the effort required is great and is placed on the back and abdominal muscles, whereas if it is lifted with the legs bent and the back straight, the effort is less and is taken by the leg and thigh muscles. These basic principles have been summarized in the 'six-point drill' of the National Safety Council (NSC).

The heights to which heavy objects have to be lifted can often be reduced by the use of a platform.

A heavy object should be carried with the arms straight, with the head close to the body and with a straight back. Changes of grip and twisting movements should be avoided. So should blind carrying, in which the load prevents the carrier from seeing in front of him. The floors or other surfaces over which the carrying is done should not be slippery.

Any protective clothing necessary for handling should be worn. In particular, the task often requires the use of safety shoes or gloves.

A single worker should not attempt to handle an object which is too heavy for him alone. He should obtain the assistance of others.

The maintenance of a fixed position is one of the most tiring tasks for the muscles. Thus even a seated task may cause muscle strain if it requires the operator to adopt awkward static positions.

In addition to recognized handling tasks, the occurrence of handling operations in such tasks as maintenance should be considered.

Handling objects requires good muscle tone. A worker should therefore be given time to tone his muscles up before being required to lift the heaviest loads if he is not used to such work.

It is important to give training in matters of handling. This is so not least because people often feel they know how to do it correctly, when in fact they do not. People often attempt from misjudgement, zeal or bravado, to handle loads which are too heavy. They should be discouraged from doing this.

A study of the effectiveness of safety training has been made by A.R. Hale (1984) which includes a case study of the effectiveness of training in handling loads. The basic principles commonly taught are those of the NSC's six-point drill mentioned earlier. The study found that conventional training tended to concentrate on injuries to the back, to the exclusion of other handling injuries, that it did not actually result in correct handling actions, and that recognition of good and bad postures was more important than action drills.

25.14.2 Hand and power tools

The proper use of hand tools is clearly essential for safety. But injuries also arise from the use of defective tools. A split hand file handle may come off and allow the file to penetrate the hand. A 'mushroomed' head on a cold chisel may loose fragments which could injure the eye. Another cause of injury is the use of the wrong tools. It is necessary, therefore, to provide suitable tools for the range of tasks to be performed, to store them securely, to maintain them properly and to have them regularly inspected by a competent person.

Guidance on the use of portable hand-held power tools includes PM 14 *Safety in the Use of Cartridge Operated Tools* (HSE, 1978) and *Pneumatic Tools—Safety in Operation*, *Safety Recommendations for the Use and Operation of Portable Pneumatic Tools* and *Recommendations for the Proper Use of Hand Held and Hand Operated Pneumatic Tools* by the European Committee of Manufacturers of Compressors, Vacuum Pumps and Pneumatic Tools (PNEUROP) (n.d.a, n.d.b, 1986, respectively). A further account is given by Bland (1977).

25.14.3 Welding

Welding operations may involve hazards to the plant and the welder. The former have been dealt with in other chapters, particularly Chapter 21, and only the latter are considered here.

Guidance on welding is given in MS 15 *Welding* (HSE, 1978) and PM 64 *Electrical Safety in Arc Welding* (HSE, 1986). Further sources of guidance are the publications of the Welding Institute (WI), the American Welding Association (AWS), the AIHA and the API. These include *Health and Safety in Welding and Allied Processes* by Balchin (1991 WI/43); the *Welding Handbook* (AWS, 7th ed 1976–/1, 8th ed. 1987–/2), the EWH series *Effects of Welding on Health* (AWS, 1979–/3, 4), *Fumes and Gases in the Welding Environment* (AWS, 1979/5) and *Fire Safety in Welding and Cutting* (AWS, 1992/13); *Arc Welding and Your Health* (AIHA, 1984/6) and *Welding Health and Safety Resource Manual* (AIHA, 1984/8); and *Safe Welding and Cutting Practices in Refineries, Gasoline Plants and Petrochemical Plants* (API, 1988 Publ. 2009). Further accounts are given by Sanderson (1969, 1977). A relevant standard is BS 1542: 1982 *Specification for Equipment for Eye, Face and Neck Protection Against Non-ionizing Radiations arising during Welding and Similar Operations.*

The principal method of welding considered here is electric arc welding, which may be done by manual, semi-automatic or fully automatic methods and may take place in a welding shop or on site.

Electric arc welding uses power supplied by transformers or motor-generator sets which are supplied by the factory electrical system or by a self-contained engine-driven generator set. The circuit has three electrical connections: the welding lead, the welding return and the welding earth.

During welding the electrode and parts of the holder are electrically live and hot, the arc gives off high intensity visible light and both infrared and ultraviolet

radiation and fumes are evolved. It is necessary, therefore, to take suitable precautions so that the operation can be done safely.

The welding connections should all be capable of carrying the full welding current. The welding lead should be robust and flexible enough for its purpose. The welding return, which is often the most neglected part, should receive equal attention. It need not be as flexible and in a workshop may be a permanent installation. The welding earth should be as near the work as possible rather than at the source of supply, although this is not always practicable. All joints in these connections should be in good condition. Where it is unavoidable that the cables are laid over rough surfaces, there should be frequent inspection for defects.

The electrode holder should be of sufficient size and should be insulated. Gloves should not be relied on to achieve insulation. If work is temporarily interrupted, the safest procedure is to render the holder electrically dead.

In the UK open circuit voltages up to 100 V are used for welding, but in certain situations, such as welding at height, in damp conditions or in vessels, this may be too high a voltage for safety. Low voltage devices can be fitted which reduce the open circuit voltage by about half. These restore the full voltage when the electrode is touched to the work so that the arc can be struck. The voltage across the arc then drops as usual to a much lower value.

Some portable welding sets, particularly semi-automatic gas shielded equipment, have hoses for gas and water supply. The equipment should not be pulled around by the cables and the hoses. Both the latter should be regularly inspected.

Proper protective clothing and equipment should be used for welding. This typically includes an apron or more extensive covering, leather gloves and a helmet which has suitable filter glass and which protects the back of the neck from other nearby arcs. Different filter glasses are required for different welding currents. A hand shield with filter glass may be used as an alternative for short periods.

Screens may be used to protect other people from the rays of the arc. Booths used for welding should have a matt finish to reduce reflected light. This is an important precaution, especially with heavy current welding and high density arcs.

There should be adequate ventilation, particularly when working in a confined space. One purpose of ventilation is to remove welding fumes. These are not particularly detrimental to health, although some fumes such as those from galvanized materials are more noxious, but exposures should be minimized. Ventilation is also needed to remove inert gases such as nitrogen, argon and carbon dioxide. The two latter are heavier than air and thus tend to accumulate in confined spaces. This is made more hazardous by the fact that the gases cannot be smelled and that the welder may be out of sight. The use of air-supplied breathing apparatus is necessary in some cases.

In welding care should be taken that hot metal does not damage equipment or set alight material, which may lead to a fire.

Since electric arc welding involves electricity, the statutory notice for electrical equipment should be posted.

25.14.4 Corrosive chemicals

Corrosive chemicals present two kinds of hazard. One is corrosion of the plant leading to failure and hence injury. The other is injury from direct contact with the chemical, usually during some operations or maintenance activity.

Accounts of the problem are given in *Safety and Management* by the Association of British Chemical Manufacturers (ABCM) (1964/3) and by Harford (1969) and E.L.M. Roberts (1977).

Chemical corrosion is hazardous if it causes leaks in the plant or a failure in features such as staircases and handrails. It is necessary, therefore, to design both the plant and the buildings or structures to resist corrosion.

The vessels and pipework of the plant itself should be designed so that they do not corrode excessively and so that the effects of corrosion such as leaks and blockages can be dealt with as easily as possible.

The plant should also have a suitable layout. Open vessels containing corrosive materials and similar hazardous features should be fenced off. Parts which may leak, such as pipe flanges, should not be located over walkways and should, if necessary, have handrails around them. Floors and other surfaces should be sloped to let spillages drain or be washed away and to avoid allowing corrosion of features such as stairways by spilled materials. The layout of the plant for corrosive materials is discussed more fully in Chapter 10.

There should be clear marking of equipment and pipework to minimize errors of identification.

The plant should be maintained to a standard commensurate with the corrosive hazard. Leakage of fluids at high pressure is particularly dangerous.

There should be regular inspection of buildings or structures which may become corroded. Items which are vulnerable or which may fail with serious consequences include stairways, ladders and handrails, high level walkways, anchor points and lifting tackle.

Adherence to systems such as the permit-to-work system and to procedures such as the procedures for line breaking or for sampling and the prompt repair of leakages and cleaning up of spillages are effective in reducing the hazard from direct contact.

The plant should be provided with showers, eye fountains, eye washes and other neutralizers as applicable.

25.14.5 Compressed air

Compressed air is widely used in plant and in workshops, and presents hazards which are often not appreciated. Guidance is given in HS(G) 39 *Compressed Air Safety* (HSE, 1990) and by Paterson (1969, 1977).

Compressed air is provided by air compressor systems and it is used in blow guns and pneumatic tools. Compressor systems are treated in Chapter 12 and pneumatic tools in Section 25.14.2.

Use is often made of compressed air from a blow gun to blow swarf, filings and chippings from equipment or machinery. The air blast needed to effect such cleaning is usually quite sufficient to blow debris into, and cause injury to, the eye.

Another practice is the use of compressed air to clean clothes or parts of the body such as the hair. This is a very hazardous procedure. Air may enter the bloodstream through cuts in the skin, possibly with fatal results, or it may cause injury to the eye, ears, nostrils

or rectum. The pressure needed to burst the bowels is quite low, about 4 psig. Moreover, it is emphasized that clothing offers no protection.

Horseplay with compressed air is likewise extremely dangerous. Air lines put down the trousers or even up the rectum have caused fatal or near-fatal injury.

The nature of the hazard from compressed air is such that it may affect not only the operator but also other people nearby.

Guidance on safer types of blow gun is given in HS(G) 39. This states that only two types are suitable, those with reduced jet velocity safety nozzles and those with air curtain safety nozzles. Whilst not foolproof, these types greatly reduce the risk. Types of blow gun nozzle which consist simply of a reduced orifice in direct line with the supply hose can be extremely dangerous and should not be used unless preceded by a tamper-proof pressure regulator.

Compressed air may also cause dust deposits to rise and form a dust cloud, thus creating the risk of a dust explosion.

25.14.6 Oxygen

As already mentioned, an oxygen-enriched atmosphere greatly increases the flammability of many materials, including clothing. Oxygen leakage from the process or from oxygen cylinders can create a hazardous situation. A relevant code on this topic is NFPA 53M: 1990 *Fire Hazards in Oxygen-Enriched Atmospheres*.

Moreover, for this reason oxygen should not be added to an oxygen-deficient atmosphere, such as that in a vessel, in order to make it breathable.

Oxygen is used in one type of self-contained breathing apparatus. It should not be used in the alternative type which uses air.

Ozone is a hazard at very low concentrations, due to its powerful oxidizing effect, the OES being 0.1 ppm. Guidance is given in EH 38 *Ozone: Health Hazards and Precautionary Measures* (HSE, 1983).

25.14.7 Inert gas

Atmospheres of inert gases which do not support respiration are common in the process industries, especially in vessels and confined spaces.

Guidance on oxygen-deficient or inert atmospheres is given in *Oxygen-Deficient Atmospheres* by the Compressed Gas Association (CGA) (1983 SB-2) and *Guidelines for Work in Inert Confined Spaces in the Petroleum Industry* (API, 1987 Publ. 2217A).

Breathing equipment for use in oxygen-deficient atmospheres must have its own air supply. The air-purifying type is not suitable.

It should be appreciated that an oxygen-deficient atmosphere can occur outside the plant as well as inside it. Accidents have occurred in which a worker standing alongside plant has been asphyxiated. The hazard is greatest if the plant has been opened up for some purpose such as repair.

25.15 Personal Protective Equipment

There are many tasks for which some form of personal protective equipment such as clothing or other equipment is necessary.

Accounts of personal protective equipment (PPE) are given in *Chemical Protective Clothing* (CIA, 1986 RC7), *Guidelines for Selection of Chemical Protective Clothing* (Schweppe *et al.*, ACGIH 1987/10), *Chemical Protective Clothing Performance Index Book* (Forsberg and Keith, ACGIH 1989/30) and *Chemical Protective Clothing* (Johnson and Anderson, 1990 AIHA/18) and by H.H. Fawcett (1965b, 1982c), C.S. Nicholson (1969), K.R. Nicholson (1976), Riddell (1977), Crockford (1980), Parson (1988) and Preece (1988). Some British Standards and National Fire Protection Association (NFPA) codes for protective clothing are given in Appendix 27.

A significant problem associated with PPE is the setting of the standards which the equipment is required to meet. This is discussed by Berry (1969, 1977).

Some tasks which may require PPE are (1) working with corrosive chemicals, (2) working with toxic chemicals, (3) working with dusts, (4) working in hot environments, (5) working in noisy environments, (6) welding, (7) fire fighting and (8) rescue.

Protective clothing should be regarded as a last line of defence. It is much preferable to remove or control the hazard, if this is practicable.

For some tasks there are specific statutory requirements that protective clothing should be worn. In the UK such requirements were rare until the 1940s but they are now quite numerous. Even where specific statutory requirements do not exist, the use of protective clothing is often necessary to comply with the HSWA 1974, Section 2.

It is the responsibility of management to specify when protective clothing and equipment are required and to provide them. The worker then has the duty to use them. If he is reluctant to do so, management is responsible for enforcing their use. The Factory Inspectorate has used the prohibition notice procedure on an individual worker to make him wear protective clothing.

According to the Act, Section 9, no charge may be levied on an employee for anything done or provided to meet a specific statutory requirement.

Some types of protective clothing and equipment are (1) body clothing, (2) gloves, (3) helmets, (4) shoes, (5) eye protection and (6) ear protection.

There is no point in providing protective clothing which is not used. In general, therefore, it is better to select practical clothing which offers a good level of protection rather than theoretically safer but more cumbersome clothing. But each case should be considered on its merits.

Protective clothing may be general issue or may be issued to an individual. The latter policy is preferable wherever it is practicable.

For some substances specific guidance is available, as exemplified by EH 27 *Acrylonitrile: Personal Protective Equipment* (HSE, 1981).

25.15.1 Eye protection

The eye is a vulnerable organ and the avoidance of eye injury is particularly important.

The Factories Act 1961, Section 65, states that eye protection may be specified in certain processes, and eye protection has been covered by the Protection of the Eyes Regulations 1974 which give a schedule of

processes for which appropriate eye protection is required. These processes include various cleaning and blasting operations using shot, water jets and compressed air, various operations involving particular tools, especially power tools, and various processes with hot metal or molten salt. Of particular relevance here is item 11, which reads:

> The operation, maintenance, dismantling or demolition of plant or any part of plant which contains or has contained acids, alkalis, dangerous corrosive substances, whether liquid or solid, or other substances which are similarly injurious to the eyes, and which has not been so prepared (by isolation, reduction of pressure, emptying or otherwise), treated or designed and constructed as to prevent any reasonably foreseeable risk of injury to the eyes of any person engaged in any such work from any of the said contents.'

These regulations are now superseded by the Personal Protective Systems at Work Regulations 1992, which deal with all types of such protection, including eye protection. Requirements for eye protection are also contained in certain other regulations.

Guidance on eye protection is given in L25 *Personal Protective Equipment at Work* (HSE, 1992) and *Protection of the Eyes* (CIA, 1990 RC22) and by Guelich (1965), Barker (1969, 1977) and Wigglesworth, 1974.

Flying objects, chemicals and radiations are the main hazards to the eye in the process industries. Flying objects come most often from the use of hand or power tools. Chemical splashes are typically caused by operations such as line breaking or sampling. Welding is the main source of injurious radiations.

The hazard to the eye from power tools such as grinding wheels is understood and the use of eye protection is normal. There is evidence that, as a result, injuries to the eye from hand tools are as frequent as those from power tools (Wigglesworth, 1974).

The general principle that personal protection should be used only if hazard elimination and control are not sufficient applies with particular force to eye protection. The main types of eye protection are spectacles, goggles and face shields.

Spectacles have either prescription or plain lenses, depending on whether the wearer does or does not wear glasses. The lenses are glass or plastic such as cellulose acetate, acrylic or polycarbonate material. For welding, filter lenses are used.

The most appropriate eye protection depends, in principle, on the task. A view which is not only widely held but is also supported by successful company systems is that the most effective approach is to issue safety spectacles to all personnel who need eye protection and to require their use. Although safety spectacles do not give total protection against all eye hazards they do give perhaps 90% protection and are more likely to be worn than some other devices. In other words, a protection which is worn is better than a superior protection which is not worn. The objective of the system based on safety spectacles is to achieve a situation where these are worn as naturally as prescription spectacles. This means that the spectacles should be fitted individually.

The alternative approaches are systems based on eye protection areas, supervisor's orders or personal judgement.

Whatever system is adopted, there are tasks for which eye protection other than safety spectacles is required. In particular, some tasks require protection not only for the eyes but for the whole face. This applies especially to persons handling corrosive chemicals or doing welding.

First aid for eye injuries is discussed in Section 25.17.

25.16 Respiratory Protective Equipment

There are a number of tasks in the process industries for which respiratory protective equipment, or breathing equipment, is necessary.

Guidance on respiratory protective equipment (RPE) is given in HS(G) 53 *Respiratory Protective Equipment* (HSE, 1990) and also in *Respiratory Protection: A Manual and Guideline* (Colton, Birkner and Brosseau, 1991 AIHA/23) and by H.H. Fawcett (1965d, 1982d), Cheffers (1969, 1977), Vanchuk (1978), Crockford (1980), Louhevaara *et al.* (1986), Stull (1987a,b), Parson (1988) and Preece (1988). Some special applications are dealt with in EH 41 *Respiratory Equipment for Use against Asbestos* (HSE, 1985) and EH 53 *Respiratory Protective Equipment for Use against Airborne Radioactivity* (HSE, 1990).

Relevant standards are BS 4275: 1974 *Recommendations for the Selection, Use and Maintenance of Respiratory Protective Equipment* and BS 4667: Part 3: 1974 *Fresh Air Hose and Compressed Air Line Breathing Apparatus.*

25.16.1 Regulatory requirements

The Factories Act 1961, Section 20, and formerly the Chemical Works Regulations 1922, Sections 6–8, require the use of approved breathing apparatus for work in vessels and confined spaces where the atmosphere may contain dangerous fumes or may lack oxygen. There are requirements for the use of respiratory protective equipment in the Control of Lead at Work Regulations 1980, the Control of Asbestos at Work Regulations 1987 and the COSHH Regulations 1988.

The use of RPE should not be a substitute for measures to maintain a breathable atmosphere. The regulations require that it be used only as a last line of defence in situations where it is not reasonably practicable to control exposure by other means.

The regulations deal not only with the situations in which RPE should be worn, but also with its suitability and specification. In essence, they require that it be suitable for use, in that it has a sufficient air supply, that it fits well and that it is worn properly. The regulations also require that the RPE should meet a laboratory test specification. For an application requiring a high level of protection this means that the HSE must approve the equipment itself and issue an Approval Certificate. For a lower level of protection it is sufficient that the equipment meet a laboratory test approved by the HSE.

25.16.2 Applications of RPE

As just stated, RPE should be used only where it is the only reasonably practicable approach. There are four main types of situation in which it is used. These are (1) temporary situations, (2) short duration situations, (3) maintenance work and (4) escape. Temporary situations are those which arise in non-routine circumstances such

Table 25.6 *Types of respiratory protective equipment (after HSE, 1990 HS(G) 53)*

A	Respirators
A1	Filtering respirators
A1.1	Disposable filtering facepieces
A1.2	Half-masks + filters
A1.3	Full face masks + filters
A2	Powered respirators
A2.1	Half-masks
A2.2	Full face masks
A2.3	Visors
A2.4	Hoods and helmets
A2.5	Blouses (half-suits)
B	Air-supplied equipment[a]
B1	Compressed air-supplied equipment
B2	Fresh air hose equipment
B2.1	Unassisted
B2.2	Manually assisted
B2.3	Power assisted
B3	Breathing apparatus
B3.1	Compressed air line apparatus: demand type
B3.2	Compressed air line apparatus: demand type with positive pressure
B3.3	Self-contained breathing apparatus: open-circuit compressed air type
B3.4	Self-contained breathing apparatus: closed-circuit compressed oxygen type

[a] HS(G) 53 classifies simple compressed air-supplied equipment in its Figure 3 in terms of (a) blouses, (b) hoods, helmets and visors, (c) half-masks, and (d) constant flow equipment, but classifies fresh air hose equipment in terms of the assistance to the air flow.

as commissioning. An important particular case is for activities in emergencies. Short duration situations may arise routinely. It is not normal for a worker to wear RPE all the time, but he may wear it routinely for certain tasks, e.g. sampling or vessel entry.

25.16.3 Types of RPE

There are two broad classes of RPE. One is the respirator, which takes in air from the workspace and filters or cleans it, removing noxious gases and vapours or dusts, before it is inhaled. It is not itself a source of air and is quite unsuitable for use where the bulk gas in the atmosphere is not breathable air but is an asphyxiating mixture.

The second class is air-supplied equipment which does have a source of clean air. This class may itself be subdivided into equipment to which air is supplied by a hose and breathing apparatus. Air for equipment supplied by hose may be compressed air or from a fresh air source. Breathing apparatus may be of the compressed air line or self-contained type.

HS(G) 53 gives the classification of RPE shown in Table 25.6. It contains an appendix giving illustrated descriptions of the main types.

25.16.4 Air-purifying respirators

The disposable facepiece or the half-mask respirator fits over the nose but does not cover the whole face. A full face-mask respirator does cover the whole face; the wartime 'gas mask' is of this type. A powered respirator has a fan to assist the flow of air through the filter.

Each type of respirator is available in three performance classifications. Thus half-mask and full face mask respirators may be of the P1, P2 or P3 specification.

The filters available for respirators are of three types: (1) filters for particular gases and vapours only, (2) filters for dusts and other particulate materials and (3) combination filters for particular gases and vapours and for dusts and other particulates.

As already stated, the air-purifying respirator differs fundamentally from the air-supplied RPE in that it is not itself a source of air and is therefore of little use unless breathable air can be drawn through it from the surrounding atmosphere. It will not sustain breathing in an asphyxiating atmosphere.

The concentration of oxygen in normal air is approximately 21%. A person breathing air with an oxygen concentration of less than about 16% may manage to do light work for a few minutes, but is likely to exhibit symptoms ranging from laboured breathing to unconsciousness or death.

Respirators are produced for military, fire fighting and industrial uses. In the former case they are commonly referred to as 'gas masks'. A respirator intended for one type of application should not be used in another.

The purifying element may work in several ways. Usually it adsorbs the gas. Alternatively, it may act as a catalyst: carbon monoxide is oxidized catalytically to carbon dioxide.

The element is designed to protect against a particular chemical or group of chemicals and should not be used for other substances. There are a number of toxic gases for which a respirator is quite unsuitable. Respirators should not generally be used against gases which have a high odour threshold or no odour at all, since odour is the only warning of failure of the respirator.

Some toxic gases are irritant to the face and for these full face protection should be used.

It is essential that respirators be kept in good condition and not held too long in stock, otherwise the air-purifying element and/or the facepiece may deteriorate. The purifying element should be replaced after use or after the elapse of a certain time according to a specified policy.

It will be apparent that, although respirators are the most convenient form of RPE and have many legitimate applications, they also have some serious drawbacks and the circumstances in which they are used should be carefully considered.

25.16.5 Simple compressed air-supplied equipment

Simple compressed air-supplied equipment is so called to distinguish it from compressed air line breathing apparatus, described below. In simple compressed air-supplied equipment the air is supplied through a hose from an independent source of compressed air. There are various types, utilizing a full face mask, half-mask, hood or blouse.

The air supplied should meet the air quality standard described below. It should come from a high quality source which is capable of meeting the foreseeable needs of those requiring to use it. It should not be drawn for the compressed air supply intended for general

works use. There should be suitable pressure reducing and pressure relief arrangements to protect the wearer from overpressure.

The hose used should comply with BS 4667: Part 3: 1974. The air line should be secured by a sturdy harness. Its route should be carefully chosen to keep it short, to allow escape and to avoid fouling and damage and it should be kept free of kinks.

Simple compressed air-supplied equipment is not breathing apparatus and it should not be used in situations where there is immediate danger to life or health; in other words, it should not be used in circumstances where an unprotected person would be rapidly overcome.

25.16.6 Fresh air hose equipment

In fresh air hose equipment the air is supplied through a hose from a fresh air source. There are various types, utilizing a full face mask, half-mask, hood or blouse.

The requirements for air quality and for hose quality and routing for compressed air-supplied equipment apply also to fresh air hose equipment. Like simple compressed air-supplied equipment, fresh air hose equipment should not be used in situations immediately dangerous to life or health.

25.16.7 Breathing apparatus

Breathing apparatus (BA) is of two types. One is compressed air line apparatus and the other is self-contained breathing apparatus. Breathing apparatus, whether of the compressed air line or self-contained type, provides the highest degree of protection and is the only type suitable for use in an atmosphere immediately dangerous to life or health.

25.16.8 Compressed air line breathing apparatus

Compressed air line apparatus is used with a full face mask or a full enclosing suit. There are two different methods of supplying the air. One is negative pressure demand in which the suction in the face mask generated by inhalation opens a demand valve allowing air into the mask. The other is positive pressure demand. With the former the pressure inside the mask is slightly below atmospheric, whilst with the latter it is mainly above atmospheric, although it can fall below at high inhalation rates.

25.16.9 Self-contained breathing apparatus

Self-contained breathing apparatus (SCBA) comes in two types. One utilizes compressed air on an open-circuit system and the other compressed oxygen on a closed-circuit system.

Open-circuit compressed air breathing apparatus utilizes a full face mask to which air is supplied from compressed air cylinders carried on the wearer's back.

Closed-circuit compressed oxygen breathing apparatus utilizes a full face mask to which oxygen is supplied from compressed oxygen cylinders carried on the wearer's back. Exhaled air is passed through a purifier which removes carbon dioxide and is recirculated.

Self-contained breathing apparatus offers the wearer mobility but requires him to carry on his back a bulky load.

Use of oxygen instead of air introduces certain problems. There may be physiological effects on the person breathing it. The flammability of material is much increased in oxygen-enriched air.

The length of time for which breathable air is supplied by self-contained breathing apparatus is typically $\frac{1}{2}$ h and 1 hour for both types, but the time for which an apparatus provides air depends on the breathing of the wearer. Heavy exertion may cause an apparatus to run out before the nominal period.

Exhaustion of the air supply is hazardous and may cause asphyxia. An adequate safety margin of time should be allowed. There is normally a timer which can be set to give warning when the time has run out.

Self-contained breathing apparatus is indispensable, but it is more complex to use than other types. Maintenance and training aspects are therefore especially important.

25.16.10 Escape breathing apparatus

A particular type of self-contained breathing apparatus is that provided for escape. Such escape breathing apparatus is intended for use over a short duration, typically less than 10 minutes, and should be used for this purpose only.

25.16.11 Air quality standard

There are air quality standards which apply to air supplied to any form of air-supplied RPE. Standards are given in BS 4275: 1974 and in HS(G) 53, Appendix 4. The latter states that: the air supplied should contain not more than 5 ppm of carbon monoxide and 500 ppm of carbon dioxide, with other impurities kept to a minimum; the air should be comfortable, being in the temperature range 15–22°C and with relative humidity no higher than 85%; and the air flow capacity should be a minimum of 120 l/min per person.

25.16.12 Selection of RPE

The procedure for the selection of a suitable RPE described in HS(G) 53 is a two-stage one. The first stage involves selection on the basis of the contaminant concentration and the second involves selection on the basis of work-related and personal factors.

The guide gives a set of charts formulated in terms of the maximum multiple of the occupational exposure limit for which a particular RPE is suitable. For example, the suitabilities of full face-mask respirators for dusts and other particulates are shown as multiple values of about 5, 13 and 800 for filter classifications P1, P2 and P3, respectively. There are separate charts for respirators for gases and vapours, respirators for dusts and other particulates, and for simple compressed air-supplied and fresh air hose equipment.

In selecting a respirator account should be taken of the suitability of the filter for the particular gas or vapour and of the time until 'breakthrough', when the filter becomes ineffective.

Work-related factors which need to be taken into account in the second stage of selection include the length of time for which the RPE is to be worn, the physical work rate, and the needs for mobility, visibility and communication.

Personal factors include medical fitness, face shape and size, facial hair, and the use of spectacles. A worker should not be subjected to additional health risks by virtue of wearing an RPE. Persons with a respiratory

disorder may find difficulty with respirators which relay on lung power to draw air through the filter.

A face mask should achieve a good fit to the face. Procedures for checking face fit are given in HS(G) 53, Appendix 5. A beard or even stubble is liable to prevent a good fit to a face mask. Where there is immediate danger to life or health, a wearer with facial hair should be provided with an alternative type such as a hood, blouse or air-fed suit.

For a wearer of spectacles the side arms tend to interfere with the seal of a full face mask and an alternative should be used such as a hood or blouse. However, spectacles worn inside these may mist over or become dislodged. Spectacles should not be worn, therefore, where the wearer would be in immediate danger to health if he removed the equipment to adjust his glasses or would be unable to leave the contaminated area at once in case of a problem.

25.16.13 Procedures for using RPE

There should be written procedures covering the situations in which RPE should be used and the actual use of the equipment, and the use should be integrated in the permit-to-work system.

The use of RPE is liable to involve a degree of discomfort and the periods for which it is required to be worn should be set with this in mind.

For a respirator, an estimate should be made of the duration of the protection provided by the filter cartridge used.

The equipment should be used in accordance with the manufacturer's instructions. It should be checked before use and should not be used if it has not been cleaned or is defective. Equipment which relies on a face seal should be given a fit test on each occasion it is used.

Where the atmosphere in an area is immediately dangerous to life or health, only breathing apparatus should be used. There should be continuous supervision of the wearer from outside the area of hazard. Either the wearer should be kept under continuous observation or should be in communication with the person supervising. Rescue equipment should be available.

Where contamination of the RPE is likely to occur due to dust or other substances hazardous to health, facilities for decontamination should be provided at the exit from the contaminated area, so that the spread of such substances is minimized.

25.16.14 Maintenance of RPE

There should be a system of records for RPE covering its storage and maintenance.

RPE for immediate use should be clean and free of defects before being put into storage and should be segregated from equipment awaiting maintenance. There should be an adequate stock of spares for items such as filters, head straps and batteries.

The maintenance required includes cleaning, disinfection, examination, repair and testing. HS(G) 53 gives details of good practice in maintenance and, in Appendix 6, of examination and testing.

25.16.15 Training for RPE

Persons involved in the use of RPE should be given suitable training. Management should have an appreciation of RPE, its applications, selection, use, maintenance and limitations. Wearers should be trained in the wearing and use of the equipment and its limitations. Maintenance personnel should receive training in the maintenance, repair and testing of the equipment.

Training should be both theoretical and practical. The former should include: the hazards of contaminants and asphyxiation and the use of RPE to control exposure; the operation, performance and limitations of the equipment; the operating procedures and permit systems which govern its use; the storage and maintenance of the equipment; and the factors which may reduce the protection which it provides.

Practical training should cover: practice in inspecting the equipment before use; obtaining a good fit to the face, where applicable; putting the equipment on, wearing it and removing it; cleaning it after use; storing it; and replacing parts such as filters and cartridges.

Training is particularly important for the types of RPE which are more complex and are used in atmospheres immediately dangerous to life or health such as self-contained breathing apparatus.

25.17 Rescue and First Aid

Effective rescue and first aid arrangements are essential in the process industries.

The Factories Act 1961, Section 61, and formerly the The Chemical Works Regulations 1922, Sections 6–14, contain various provisions for rescue and first aid.

The responsibility for the provision of these services should be clearly defined. There are some features, such as rescue equipment, which might, in principle, come under either the safety, the fire or the medical department.

All rescue and first aid equipment should be located with care and properly maintained. Personnel should be fully trained in its use.

25.17.1 Rescue

An account of general rescue methods is given in *The Light Rescue Handbook* by the Ministry of Defence (MoD, 1989a) (the MoD *Rescue Handbook*). Rescue from confined spaces is treated in *Recommendations to Facilitate Rescue from Confined Spaces* (EEUA, 1962 Doc. 12). A further account is given by Walters (1977).

There should be a rescue system which is capable of handling all reasonably foreseeable situations which may arise on a process plant. Frequently this function is performed by the works fire services, supplemented if necessary by the local authority fire services.

Rescue apparatus such as stretchers should be provided at strategic points.

Arrangements for rescue are also part of certain routine tasks such as entry into vessels or confined spaces and of some special operations such as hot tapping.

The MoD *Rescue Handbook* is oriented to rescue tasks arising from both natural and man-made disasters such as earthquakes and hurricanes and road and rail crashes. It deals with: the aims of rescue; the organization of the rescue team; the responsibilities of the team leader; personal and rescue equipment; searching for casualties; the five stages of rescue (surface casualties, lightly damaged buildings, likely survival points, selected debris removal, and general debris clearance); recovery of the

dead; recovery of valuables; building construction; levering and jacking; strutting and shoring; repairs to utilities; rope and wire bonds; knots and lashings; and thermal image cameras.

25.17.2 First aid

Regulatory requirements for first aid are given in the Health and Safety (First Aid) Regulations 1981. COP 42 *First Aid at Work. Health and Safety (First Aid) Regulations 1981* (HSE, 1990) is the relevant ACOP. The relevant manual is the *First Aid Manual* of the St John Ambulance Association (1992), the official manual of the three leading organizations in the UK in this field, the St John Ambulance Association, the St Andrews Ambulance Association and the British Red Cross. First aid is also treated in *First Aid Manual for Chemical Accidents* (Lefevre, 1989 ACGIH/32) and *Industrial First Aid: Reference and Training Manual* (ACGIH, 1991/64) and by Lord Taylor (1967), Cameron (1969, 1977) and McKenna and Hale (1981). Also relevant is *Emergency Care for Hazardous Materials Exposure* (Bronstein and Currance, 1988 ACGIH/19).

The requirements of the First Aid Regulations are largely contained in Regulation 3. This requires an employer to make provisions for first aid by providing suitable equipment and facilities and by appointing suitable persons. These appointed persons have to possess a first aid certificate from an organization recognized for this purpose by the HSE and receive refresher training at specified intervals.

The ACOP deals under Regulation 3 with: different work activities needing different provisions; the applicability of, and provision of first aider cover for, situations when access to treatment is difficult, employees work away from employer's premises or employees of more than one employer work together; provision for persons other than an employer's own employees and for trainees; first aid equipment and facilities, first aid boxes and kits, travelling first aid kits, supplementary equipment, first aid room and equipment; suitable persons; criteria for deciding adequate and appropriate provisions for first aiders; number of employees and appointed persons; the recruitment and selection of first aiders; appropriate training for first aiders; access to skilled advice; recording first aid treatment; approval of first aid courses and qualifications; refresher courses; first aid training where specific hazards exist; emergency first aid training; first aid trainers and examiners; first aid examinations; and training of first aid lay trainers.

The number of first aiders required is specified in the ACOP as a minimum of one per 50 employees, a figure which applies to low risk situations. In hazardous situations the employer should assess whether a higher proportion of first aiders is required.

Subjects to be included in the syllabus for first aid training given in the ACOP include (1) resuscitation, (2) treatment and control of bleeding, (3) treatment of shock, (4) management of the unconscious casualty, (5) contents of first aid boxes and their use, (6) purchasing first aid supplies, (7) transport of casualties, (8) recognition of illness, (9) treatment of injuries to bones, muscles and joints, (10) treatment of minor injuries, (11) treatment of burns and scalds, (12) eye irrigations, (13) poisons, (14) simple record keeping, (15) personal hygiene in treating wounds with reference to hepatitis B and human immunodeficiency virus (HIV) and (16) communication and delegation in an emergency.

It is necessary to have a first aid system which can deal with the types of injury likely to be encountered on the plant, and where there are special hazards first aiders should also receive additional training in respect of these. Normally first aiders in process plants are drawn from the process and maintenance personnel.

First aid equipment which should be provided includes first aid boxes and resuscitation apparatus. There should also be showers and eye wash equipment to deal with injuries from corrosive chemicals.

Showers are effective provided they are used, but there are certain practical problems. Measures need to be taken to ensure that the water supply is not frozen or turned off at a hand valve. And the reluctance of workers to make use of showers when fully clothed may have to be overcome by drills.

Guidance on first aid for eye injuries is given in *Protection of the Eyes* (CIA, 1990 RC22). Eye wash equipment includes eye wash fountains, pre-packed sterile washes, and eye wash bottles. The latter are a last resort, and are not supported by the ACOP.

Eye injuries from corrosive chemicals should preferably be dealt with by irrigation with water, using plenty of water and continuing for a long time. If sterile washes or eye wash bottles are used, they should contain an adequate volume. The CIA recommends, for example, for these two types of wash volumes of at least 500 ml and 1 l, respectively.

Information is available also on first aid for particular chemicals. Materials safety data sheets may include such information. The CIA *Codes of Practice for Chemicals with Major Hazards* and related publications give guidance on first aid.

In some situations there is a danger that the first aider may himself be injured, and precautions should be taken to ensure that this does not happen. Cases mentioned in the ACOP include casualties from electric shock, chemical burns and gassing. It states that in a case of electric shock the current should be switched off before the casualty is touched or, if this cannot be done, the first aider should stand on dry insulating material and free the casualty from the electrical source with a wooden or plastic implement. Where the casualty has a chemical burn, the first aider should avoid contaminating himself with the chemical. With a casualty who has been gassed, the use of suitable protective equipment is advised.

25.18 Notation

Section 25.7

Section 25.7.3

A area of opening (m^2)
Q volumetric air flow (m^3/s)
V inward superficial air velocity (m/s)

Section 25.7.4

A face area of hood (m^2)
L length of hood (m)
V capture velocity at distance X (m/s)
V_o superficial velocity at face of hood (m/s)
W width of hood (m)

X distance from hood (m)
α, β indices

Section 25.7.7
A_f free area of discharge (m^2)
C_d coefficient of discharge
K constant
Q volumetric flow (m^3/s)
V_x centre line velocity at distance X (m/s)
X distance along centre line (m)

Section 25.9
A, B, C constants in the Antoine equation
M molecular weight
p_i partial pressure of component i
p^o vapour pressure
p_i^o vapour pressure of component i
P total pressure
T absolute temperature
x_i concentration of component i (mole fraction)
ρ_g density of gas

26 Accident Research

Contents

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Accidents on chemical plants may hazard the process, the personnel or both. Research on accidents is relevant, therefore, both to accidents which result in property damage and those which cause personal injury.

Accident research as a discipline tends to concern itself primarily with those accidents in which people are involved. It is primarily concerned, therefore, with injury to personnel. But it does involve the study of the total accident situation. Often it is a matter of chance whether this situation hazards the process or the people. Clearly accident research is closely related to work in other fields such as human factors and, in particular, human error.

Accounts of accident research include *Occupational Accident Research* (Kjellen, 1984), *Information Processing and Human–Machine Interaction* (Rasmussen, 1986), *Individual Behaviour in the Control of Danger* (A.R. Hale and Glendon, 1987) and *Human Error* (Reason, 1990). Many of the classic papers in the field are given with commentary in the collection *Accident Research, Methods and Approaches* (Haddon, Suchman and Klein, 1964).

Much work on the subject is concerned with areas which are not of prime interest here, such as accidents to children, accidents in the home and traffic accidents.

In addition to work on personal accidents, it is convenient to deal here briefly with some principal research programmes on, and test sites for, major hazards.

Selected references on accident research are given in Table 26.1.

Table 26.1 *Selected references on accident research.*

E. Farmer (1932); Gordon (1949); Paterson (1950); Kerr (1957); Sheldon (1960); Rapoport (1961); Suchman (1961); Haddon, Suchman and Klein (1964); Surry (1969a,b); A.R. Hale and Hale (1970, 1972); Ramsey (1973); Carr (1975); Hendry (1975); Pickbourne (1975); HSE (1976d, 1993a); Smillie and Ayoub (1976); Verhaegen *et al.* (1976); Saari (1977); Kjellen (1984); Leplat (1985, 1987); Pastorino *et al.* (1986); Rasmussen (1986); A.R. Hale and Glendon (1987); Beckers (1993)

Classification of accidents
HM Chief Inspector of Factories (annual); California State Department of Health (1953–57); ILO (1961); HSE (1983c, 1986c, 1992b)

Indices of harm
Solomon and Alesch (1989)

Accident models (see Table 2.1)

Accident proneness
Greenwood and Woods (1919); E. Farmer and Chambers (1926, 1939); Newbold (1926); E. Farmer (1932); Tillman and Hobbs (1949); Arbous and Kerrich (1953); Suchman and Scherzer (1960); Cresswell and Froggatt (1963); L. Shaw and Sichel (1971); Schafer (1973a); Cazamian (1983)

Judgment, risk-taking
J. Cohen and Hansel (1956); J. Cohen, Dearnaley and Hansel (1956, 1958); Fortenberry and Smith (1981)

Risk homeostasis
McKenna (1975, 1985); Wilde (1978, 1982a,b, 1985, 1988); Shannon (1986); J.G.U. Adams (1988); Janssen and Tenkink (1988)

Human error (see Table 14.10)
Reason (1977, 1979, 1986, 1987a,b, 1990, 1991)

Slips, trips and falls
Sheldon (1960b); P.R. Davis (1983); Manning (1983); Buck and Coleman (1985); Tisserand (1985)

Road accident research
I.D. Brown (1990b); Reason *et al.* (1990); Rumar (1990); Wagenaar and Reason (1990)

Major hazards research
Brugger and Wilder (1975b); Buckley and Weiner (1978); Schneider, Lind and Parnarouskis (1980); Blackmore *et al.* (1981); Benson and Sinclair (1982); Bless (1982); Bello and Romano (1983a); Desteese and Rhoads (1983); Puttock, Colenbrander and Blackmore (1983); Johnston (1984, 1985); McQuaid (1984b, 1991); Roebuck (1984 LPB 58); Anon. (1985bb); Koopman and Thompson (1986); Quarantelli, Dynes and Wenger (1986); Schnatz (1986); Anon. (1987h); Closner (1987b); Rubin (1987); Mellor *et al.* (1988); Thomson and von Zahn-Ullman (1988); CEC (1989); Teja (1989); Carmody (1990a); Shortreed (1990); Institute for Systems Engineering and Informatics (1991a,b); Michot, Bigourd and Pineau (1992); Storey (1992); Cole and Wicks (1994)
Research facilities: FPA (CFSD OR 5, 1991 CFSD OR 6); HSE (1983/14); Le Diraison and Bailleul (1986); Redman (1986a); British Gas (1988 Comm. 1381); Flood and Stephenson (1988); Groothuizen (1988); Clerehugh (1991); D.C. Bull and Strachan (1992); CMI (1992)

26.1 General Considerations

The development of accident research has shown that there are a number of serious pitfalls in the investigation of accidents. There is a tendency for a particular feature to be studied as a possible cause of accidents and there is frequently a bias in favour of this feature. Often no information is given on any work with a control group.

This situation was contrasted with that in medical work in a classic paper by Gordon (1949), who suggested that the approach taken in epidemiology is applicable to accident research. The epidemiology model, which is described below, has been widely used in work on accidents.

26.2 Definition of Accidents

The question of what actually constitutes an accident is worth at least brief consideration. It has been considered by Suchman (1961), who distinguishes three defining

characteristics: (1) degree of expectedness, (2) degree of avoidability and (3) degree of intention. An event is more likely to be classed as an accident if it is unexpected, unavoidable and unintended.

Other secondary characteristics are (1) degree of warning, (2) duration of occurrence, (3) degree of negligence and (4) degree of misjudgement. Classification of an event as an accident is more probable if it gives little warning and happens quickly and if there is a large element of negligence and misjudgement.

It is suggested, however, by Suchman that as knowledge increases an event is more likely to be described in terms of its causal factors and less likely to be classed as an accident.

26.3 Classification of Accidents

Much work on accidents is concerned with accident statistics. These statistics are based on an accident classification of some kind. Accident classifications are therefore quite important. Unless a classification contains a particular category which is of interest, there is no means of retrieving information on it.

There are a number of standard accident classifications. These include the classification used by the HSE in its annual *Health and Safety Statistics*, published in the *Employment Gazette* and that used in the annual *Yearbook of Labour Statistics* published by the International Labour Office. Relevant standards are the American National Standards Institute (ANSI) Z16 series.

26.4 Causes of Accidents

The main aim of accident research is to understand accidents so that they can be prevented. The attempt to understand an accident is often equated with the search for its cause.

The concept of the cause of an accident, however, has become somewhat discredited. In accident investigation an administrative requirement to report a single cause usually does not do justice to the complexity of the situation. In accident research there has been much criticism of work which isolates and overemphasizes a particular factor.

It is more acceptable, therefore, to regard an accident as arising from a particular combination of factors rather than from a single cause. There is thus a tendency to consider relationships between variables rather than causes.

While this approach is undoubtedly correct in general, the danger is that the accident situation then appears incredibly complex and the attempt to understand it hopeless. The work of Rapoport (1961) provides something of an antidote to this. As he points out, the scientific technique of isolating the influence of one variable by controlled experimentation has been enormously fruitful and it should not be lightly abandoned.

Rapoport distinguishes between specific and non-specific causes both in the field of disease and in that of accidents. Progress in control of disease has come both from specific factors (e.g. vitamins), and non-specific ones (e.g. public hygiene).

Although much work on accidents is of a statistical nature, the value of the descriptive approach should not be underestimated. The work of Sheldon (1960) on accidents to old people involving falls has been cited as classic in this regard.

The investigation of accidents is dealt with in Chapter 27, which describes an illustration of an accident investigation given by Houston (1971). The investigation does not aim to find a single cause, but rather to discover the many factors which contribute to the accident.

26.5 Accident Models

Recognition of the complexity of accidents has led to the development of a number of accident models. A particular model of the accident situation is that derived from epidemiology, following the work of Gordon (1949). The factors involved in an accident are defined as follows: (1) host, (2) agent and (3) environment. Although this model derives from medical work, it has been applied in many other fields.

The main agent in an accident is usually some form of energy which inflicts physical damage. Accidents not accounted for by energy have as an agent a toxin, which is the other principal agent.

A distinction is made between an agent and the vehicle for that agent. In an accident from a falling spanner, the agent is energy and the vehicle is the spanner.

Another model of the accident situation, which draws both on Gordon's model this one and on fault trees, is that developed by Houston (1971, 1977). In this model a driving force is activated by a trigger so that through some form of contact process it causes injury or damage to a target.

A second group of models is based on the concept that it is possible to define for a system a 'normal operating state', and hence deviations from that state, and that such deviations are associated with danger. The models of G.L. MacDonald (1972) and Kjellen (1983) exemplify this group. Figure 26.1 by Hale and Glendon illustrates MacDonald's model.

A third group of models is based on human information processing. They include those of Surry (1969b), A.R. Hale and Hale (1970) and A.R. Hale and Glendon (1987). The models of Surry and of Hale and Hale are both formulated in terms of perception, cognition and physiological response, or action. That of Surry is in two parts, the first dealing with the danger build-up and the second with the danger release or emergency. Each part has a similar structure, that for danger build-up being:

Perception	Warning of danger build-up?
	Perception of warning?
Cognitive process	Recognition of warning?
	Recognition of avoidance mode?
	Decision to attempt to avoid?
Physiological response	Ability to avoid?

Another important model in this group is that of Rasmussen (1986) based on the distinction between knowledge-based, rule-based and skilled activity. As characterized by A.R. Hale and Glendon (1987), following Leplat (1985), these three levels of function correspond at the cognitive level to interpretation, identification and observation/activation and in terms of

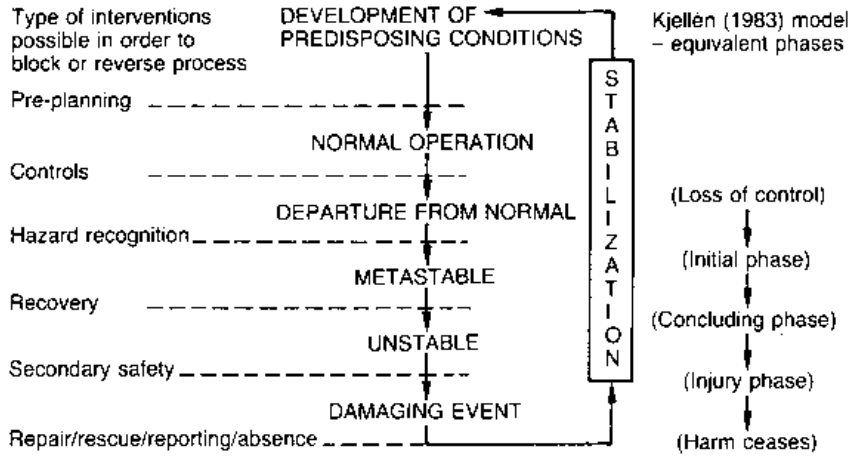

Figure 26.1 *Scheme illustrating accident models of MacDonald and Kjellen (A.R. Hale and Glendon, 1987 (reproduced by permission of Elsevier Science Publishers); after G.L. MacDonald (1972) and Kjellen (1983))*

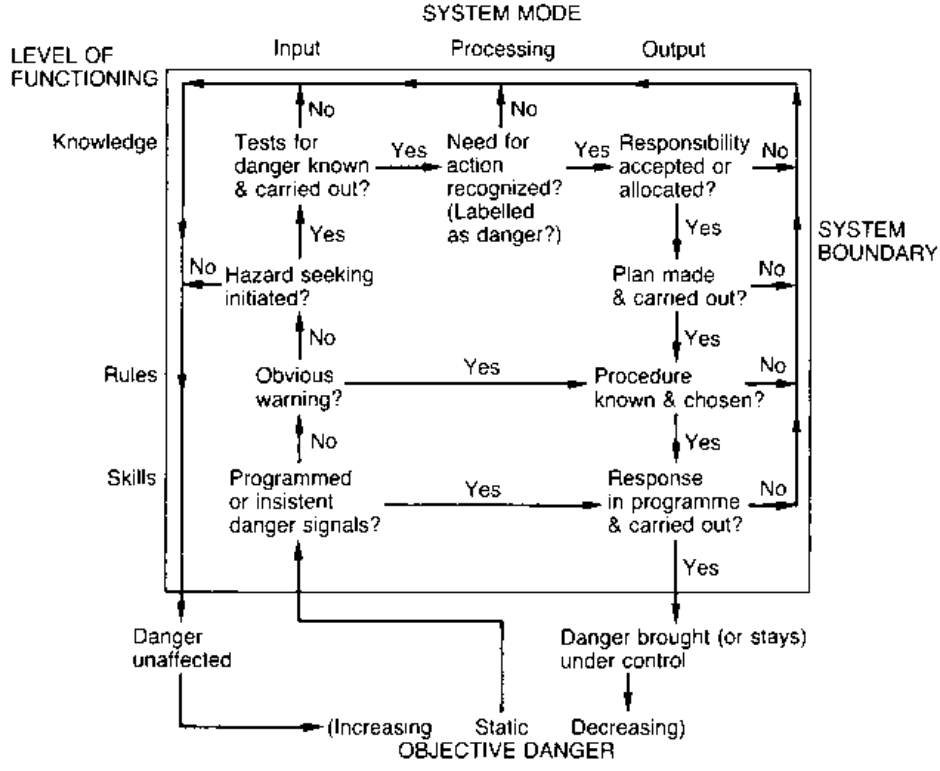

Figure 26.2 *'Behaviour in the face of danger' accident model (A.R. Hale and Glendon, 1987 (reproduced by permission of Elsevier Science Publishers))*

behaviour to evaluation/task definition, procedure and execution, respectively. The Rasmussen model is described in more detail in Chapter 14.

A model which draws on the foregoing models is the 'behaviour in the face of danger' model of A.R. Hale and Glendon (1987) shown in Figure 26.2. This has the general structure of Rasmussen's model but amplifies it

using stages drawn from Surry's model. The model shows what has to occur if the danger is to be averted. In other words it is a prescriptive model. The text by Hale and Glendon is an exploration of the factors affecting this behaviour and of the extent to which the behaviour is likely to lead to a successful outcome.

Other models, reviewed by Mill (1992), include those of the Institut National de Recherche sur la Securite (INRS) in France, the Occupational Accident Research Unit (OARU) in Sweden and the International Loss Control Institute (ILCI) in Georgia. The INRS model represents an accident as a deviation in the normal work situation and has a fault tree structure. The OARU model is intended for investigation of single person injuries and represents the accident as a chain of deviations. The ILCI model is a five layer model which progresses from basic causes in management deficiencies and progresses through to the immediate causes.

A number of other accident models, drawn mainly from the literature on process safety rather from than the psychological literature, are described in Chapter 2.

The contribution of human factors, and in particular the work situation, to accidents is considered in Chapter 14.

Table 26.2 *Prime causes of accident liability in an industrial investigation after Viteles*

Prime cause	*Percentage of cases*
Faulty attitude	14
Failure to recognize potential hazard	12
Faulty judgement of speed and distance	12
Impulsiveness	10
Irresponsibility	8
Failure to keep attention constant	8
Nervousness and fear	6
Defective vision	4
Organic disease	4
Slow reaction	4
High blood pressure	2
Senility	2
Worry and depression	2
Fatigability	2
Improper distribution of attention	2
Inexperience	2
Miscellaneous	6

26.6 Accident Proneness

The idea that certain people are accident prone is quite an ancient one. In fact the accident prone individual is a classic comic character. Accident proneness as a concept in accident research, however, dates from the classic paper of Greenwood and Woods (1919) of the Industrial Fatigue (later Health) Research Board on accidents to industrial workers. The interwar period saw a number of publications on various aspects of accident proneness by investigators at the boards, in particular those by Newbold (1926) and E. Farmer and Chambers (1939).

The fact that an individual has an above-average number of accidents does not in itself necessarily mean anything. It can be shown from the Poisson distribution that on the basis of chance alone there will be individuals who have quite large numbers of accidents. It is accidents that cannot be explained in this way which have given rise to the concept of accident proneness.

The terminology associated with the problem of the variation in accident rate between individuals tends to be a source of confusion. Accident repetition describes the observed fact that an individual has suffered an above-average number of accidents and that this is statistically significant. Accident proneness refers to a higher than average susceptibility to accidents which arises from psychological factors and tends to be permanent. Accident liability is a broader term describing an above-average accident rate which may be due to many factors, including work situations and personal stresses and which tends to be temporary. It is emphasized, however, that authors in this field have been criticized (e.g. Arbous and Kerrich, 1953) for lack of definition and consistency in their use of terms.

Greenwood and Woods (1919) showed that some industrial workers have more accidents than would be expected from chance alone, using the Poisson distribution. In other words, they established the fact of accident repetition. They offered as an explanation a theory of unequal liability to accidents, but did not themselves go so far as to suggest one of accident proneness.

These findings were confirmed in further work by Newbold (1926), who suggested that there might be a psychological explanation for them.

The phenomenon of accident repetition has subsequently been confirmed by numerous workers, many of whom have gone beyond the original investigators' more conservative conclusions to develop a theory of accident proneness.

An activity which has been studied particularly is driving (e.g. E. Farmer and Chambers, 1939; Tillman and Hobbs, 1949; Cresswell and Froggatt, 1963; L. Shaw and Sichel, 1971). Farmer and Chambers investigated driver accidents and concluded that accident proneness was an established fact. Yet the only significant correlation obtained between accident rate and individual characteristics was in tests on aesthetokinetics rather than on personality.

The concept of accident proneness has been severely criticized by Arbous and Kerrich (1953), while Suchman and Scherzer (1960) have given an evaluation of its status. The conclusion drawn is that accident proneness is difficult to establish, but that accident liability is a more acceptable concept. Accident liability may be connected with such factors as the work situation or stress, is usually temporary and does not depend primarily on personality traits.

The investigation of accident liability may in fact be a fruitful way of reducing accidents. An example is the work of Viteles at the Cleveland Railway Company (Arbous and Kerrich, 1953). He identified 50 individuals with accident liability and, taking a clinical approach, analysed the cases individually. The prime causes of accident liability which he identified are shown in Table 26.2. Various measures, including medical treatment, systematic instruction and increased supervision, were

taken. As a result, the accident rate was almost halved. This approach requires, of course, a great deal of effort.

In a further review, Cazamian (1983) takes it as established that certain individuals do have repeated accidents, but treats this as an acquired susceptibility rather than a inherent predisposition. Individuals may enter and leave the group of accident repeaters. Some factors can be identified which increase the susceptibility to repetition. Accidents are more common among young workers than mature adults, among those who lack training and experience, and among those who are ill.

26.7 Risk-taking

Some accidents occur because people consciously take risks. In a given case the risk is generally judged to be small, but it is a finite risk nevertheless, and occasionally such behaviour results in an accident.

26.7.1 Risk homoeostasis

It is sometimes argued, particularly in relation to activities such as car driving, that there is a certain level of risk which people accept and that if physical measures are taken to reduce this risk, such as improved traffic engineering or vehicle crash resistance, the effect of these measures is cancelled by changes in individual behaviour so that the end result is that the risk remains the same.

A formal theory of risk homoeostasis has been given by Wilde (1978, 1982a,b, 1985, 1988). According to this theory the loss due to road accidents per unit time is the output of a closed loop process in which the set-point is the target level of risk.

The concept of risk homoeostasis does not imply that all measures to improve road safety are doomed to failure. A distinction is drawn between physical and motivational measures. The latter act to influence the target level of risk and can indeed be effective. The theory is pessimistic, however, on the effectiveness of non-motivational measures.

A critique of the theory of risk homoeostasis has been given by McKenna (1975, 1985).

The measure of effectiveness in this debate is important. It is common ground that physical measures can reduce the accident rate per unit distance covered. It is argued, however, by Wilde that they have little effect in reducing the accident rate per unit driving time.

26.7.2 Risk judgement

Another type of situation which can also lead to accidents occurs when there is misjudgement of the risk. In relation to such accidents a distinction has been drawn by J. Cohen, Dearnaley and Hansel (1956) between judgement and capability. They investigated the ability of bus drivers to drive a bus through a narrow opening. The work distinguished between lack of success due to misjudgement of the width of the opening and inability to drive the bus through it. In some cases a generally capable driver would try to drive through an opening which was narrower than the bus itself. Obviously these two causes of failure have different implications for training.

26.8 Human Error

Work on the psychology of human error is exemplified by the work of Reason, described in *Human Error* (Reason, 1990) and in other work (Reason, 1977, 1979, 1986, 1987a,b, 1991). One aspect of this work is the recognition that many accidents occur due to absent-mindedness and that, whilst in the vast majority of cases the consequences of such absent-mindedness are not serious, in a proportion of cases they are.

Table 26.3 *Classification and examples of actions-not-as-planned (after Reason, 1979)*

A Proportion of errors in each class

1. Discrimination failures (11%)
   - 1.1 Perceptual confusions (objects confused are physically similar)
   - 1.2 Functional confusions (objects confused are functionally similar)
   - 1.3 Spatial confusions (objects confused are close together)
   - 1.4 Temporal confusions (time is misperceived and inappropriate actions initiated)
2. Program assembly failures (5%)
   - 2.1 Behavioural spoonerisms (program elements are reversed)
   - 2.2 Confusions between currently active programs
   - 2.3 Confusions between ongoing and stored program
3. Test failures (20%)
   - 3.1 Stop-rule overshoots (actions proceed beyond intended end-point)
   - 3.2 Stop-rule undershoots (actions cease before their intended end-point)
   - 3.3 Branching errors (initial sequence of actions is common to two different routines and wrong branch is taken)
   - 3.4 Multiple side-tracking (subject is apparently diverted from original intention by series of minor side-steps)
4. Subroutine failures (18%)
   - 4.1 Insertions (unwanted actions are added to a sequence)
   - 4.2 Omissions (necessary actions are left out of a sequence)
   - 4.3 Misordering (actions carried out are correct but in wrong order)
5. Storage failures (40%)
   - 5.1 Forgetting previous actions
   - 5.2 Forgetting discrete items in plan
   - 5.3 Reverting to earlier plans
   - 5.4 Forgetting the substance of plan

B Examples of actions-not-as-planned

1.1 'I put my shaving cream on my toothbrush'

1.2 'There were two objects before me on the draining board: a cloth and a container of cleaning fluid which I normally keep in the bathroom but had brought into the kitchen to use. I decided to return the cleaning fluid to its place in the bathroom, but set off with the cloth in my hand instead'

1.3 'I turned on my electric fire instead of my transistor radio which was on the floor near it'
1.4 'When I got up on Monday morning, I found myself putting on Sunday's sweater and jeans instead of my working clothes'
2.1 'I unwrapped a sweet, put the paper in my mouth and threw the sweet in the waste paper basket'
2.2 'My office phone rang. I picked up the receiver and bellowed "Come in" at it'
2.3 'I fetched a box of matches to light the electric fire'
3.1 'I brought the milk in from the front step to make myself a cup of tea. I had put the cup out previously. But instead of putting the milk into the cup, I put the bottle in the fridge'
3.2 'I was just about to step into the bath when I discovered that I still had on my underclothes'
3.3 'I intended to drive to Place X, but then I "woke up" to find that I was on the road to Place Y'
3.4 'I went upstairs to sort out and fetch down the dirty washing. I came down without the washing having tidied the bathroom instead. I went upstairs again to collect the washing, but somehow got side-tracked into cleaning the bathroom. I forgot all about the washing until I returned to the kitchen where the washing machine was pulled out in readiness'
4.1 'I came out of the sitting room in the daytime and flicked on the light as I left the room'
4.2 'I filled my electric kettle with water, plugged the lead into the back of the kettle and switched on the wall socket. When the kettle failed to boil I discovered I had not inserted the plug into the wall socket'
4.3 'Sitting in the car about to leave work, I realized I had put the car into gear and released the handbrake without first starting the engine'
5.1 'I started to walk home and had covered most of the distance when I remembered I had set out by car'
5.2 'I had intended to post a letter while I was out shopping but when I got home I found I still had the letter in my pocket'
5.3 'I decided to make some pancakes for tea. Then I remembered we didn't have any lemons so I decided not to bother. Five minutes later I started getting together the ingedients for pancakes, having completely forgotten my change of mind'
5.4 'I went upstairs to the bedroom, but when I got there I couldn't remember what I came for'

An undesired outcome may occur either because the actions do not go as planned or because the plan is inadequate. It is with the first of these causes, 'actions-not-as-planned', that the work is concerned.

Reason conducted an experiment in which 35 subjects kept a diary of their actions-not-as-planned over a 2-week period. The classification of these errors and the proportion of errors in each main class are shown in Section A of Table 26.3, while Section B gives specific examples.

The classification is based on a computer program model of human activity. The discrimination errors are failures in classification of the inputs. The program assembly errors involve use of inappropriate subroutines. The test failures refer to failure to check on the progress of a sequence or to selection of an incorrect branch. The subroutine failures involve insertion into, omission from or misordering within a sequence. The storage failures are forgetting or misrecalling plans and actions.

Reason outlines a number of concepts which may help to explain the results obtained. Skilled performance involves switching between open and closed loop modes of control. Typically a large part of a task or series of tasks may be carried out under open loop control, but it is necessary to revert to closed loop control at certain critical decision points. A failure to make the necessary switch at the appropriate moment is likely to result in an error.

In some cases a motor program sequence shares a common subsequence with another sequence, but there is a critical decision point where it diverges from this second sequence. This is a situation particularly likely to lead to error.

Some motor programs appear to acquire a strength which causes them to be activated contrary to the current plan. This is likely to apply particularly to a program which has been used frequently or recently.

Reason goes on to propose certain hypotheses concerning such errors. He suggests that test failures occur when a critical decision point is reached while still under open loop control and where the strengths of the two motor programs are markedly different, and that if an error occurs it is likely to involve the unintended activation of the strongest motor program beyond the node.

Another hypothesis is that storage failures in the execution of a sequence are associated with some counting mechanism in the motor program which checks off the actions as they are performed. It appears that on occasion this counter is unable to distinguish between planned actions and others which are similar in duration and degree of activity, so that if an interruption occurs the program resumes at the wrong point.

In tasks such as maintenance a large proportion of the errors involve omission. The practical application of the work described points to the provision of memory aids which assist the worker to remember which stage of the sequence he has reached.

This work leads to the distinction made by Reason (1990) between slips, lapses and mistakes. In essence, a slip is either an error in implementing a plan or an unintended action, a lapse is an error in which the intended course of action is not executed due to a failure of memory, and a mistake is an error in establishing the correct course of action.

26.9 Social Factors

The effect of physical features of the environment on accidents is readily appreciated. Less obvious, but often as important, is that of its social aspects. Social factors are effective in reducing accidents (1) if the socially approved behaviour minimizes accidents and (2) if individuals adhere to that behaviour.

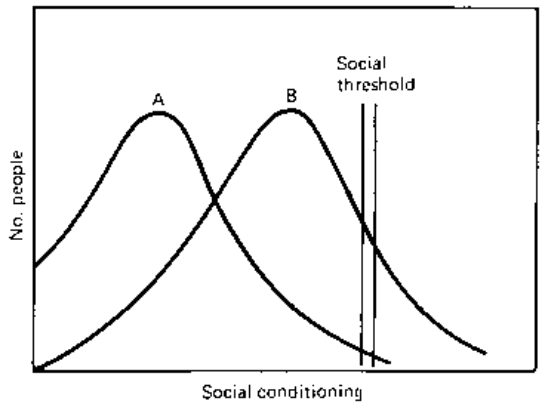

Figure 26.3 *Effect of social factors in behaviour affecting accident rates*

The effect of individual deviation from the approved standard has been considered by Paterson (1950). The basic argument may be illustrated by reference to Figure 26.3, which shows on the horizontal axis the strength of group conditioning, decreasing away from the origin, and on the vertical axis the number of people who exhibit that degree of conditioning. It is assumed that the optimal type of behaviour which minimizes accidents corresponds to that given by the highest degree of group conditioning. Curve A represents a highly disciplined society with a low mean. The discipline may be due to the harshness of nature or to the social and political system. Curve B corresponds to a less disciplined society with a high mean. Also shown in the figure is the social threshold, which is the point at which the deviation from optimal behaviour results in marked increase in accidents. If the socially approved behaviour is optimal in reducing accidents, then clearly there will be more accidents in a society where there is greater individual deviation.

It cannot be assumed, however, that social pressures always tend to reduce accidents. On the contrary, the expectations of a small peer group may well run in the opposite direction and it is often this influence which is strongest. Thus the behaviour laid down in company safety procedures may be assumed to reduce accidents. But certain types of peer group pressure may increase them. Examples are neglect of permit-to-work procedures, failure to wear protective clothing and horseplay among apprentices.

26.10 Accident Prevention

Measures to prevent energy causing injury or damage may be based on the following four principles: (1) reduction of the energy available, (2) modification of the release of the energy, (3) separation by distance and (4) separation by a barrier.

Accident models such as that of Houston (1971, 1977) are useful in analysing potential accident situations and identifying appropriate preventive measures.

Accident prevention measures are not infrequently brought in without adequate understanding of the problem and without sufficient evaluation. Such measures are likely to be relatively ineffective. There is a tendency to believe that they must be better than nothing. But often they are an obstacle to progress, because they give the impression that something is being done about the problem.

This contrasts with the very thorough trials which are made on the effectiveness of drugs in countering disease. Proper evaluation is necessary for proposed accident prevention measures also. This again is in line with the more quantitative approach which characterizes loss prevention. The practical application of this principle is seen in the work of the Road Research Laboratory on the evaluation of road safety.

26.11 Safety Training

Most prescriptions for the prevention of accidents lay much emphasis on training, and rightly so. It is necessary, however, that the training be effective.

A study of the effectiveness of safety training by A.R. Hale (1984) found relatively little previous work on the topic. The essential finding of the study is that, unless effort is invested in analysing the problem and defining the training requirements, the training is liable to be ineffective and to get the activity a bad name. The author quotes the *Robens Report* (Robens, 1972) which states: 'Most people are agreed that safety training is of vital importance. There is no unanimity about what in practice should follow from that proposition.'

The requirements for training found in the legislation by the author are patchy, with power presses governed by a detailed training schedule whilst injection moulding machines have no specific provision. There are requirements of competence for drivers of coal mine face conveyors, but not for those of fork lift trucks.

The author describes a case study of the effectiveness of safety training in the handling, lifting and carrying of loads. Details of this study are given in Chapter 25. In brief, the investigation found that the training studied was not effective and that recognition of good and bad postures was more important than action drills.

26.12 Major Hazards

Research on major hazards is described throughout this book, particularly in Chapters 15–17 on emission and dispersion, fire and explosion. The treatment here is confined to an indication of some of the major experimental programmes and the sites where they have been conducted.

Large-scale experimental trials on dense gas dispersion have been conducted in the UK at Porton Down (Picknett, 1981a–c), Maplin Sands (Puttock, Colenbrander and Blackmore, 1983) and Thorney Island (A.G. Johnston, 1984, 1985; McQuaid, 1984b) and in the USA at China Lake, California (Ermak *et al.*, 1983), and at the Nevada Test Site (Koopman and Thompson, 1986).

Large-scale trials on fire phenomena have been performed at the Health and Safety Executive's (HSE) Explosion and Flame Laboratory at Buxton. This includes work on pool fires, fireballs and engulfing fires (A.F. Roberts, 1987; McQuaid, 1991).

Other work on fires has been done at Shell sites and at the British Gas sites at Fauld and at Spadeadam in co-operative projects involving a number of companies, including in particular trials on jet flames and on fire insulation. The Maplin Sands work on dense gas dispersion included trials on vapour cloud fires.

Explosion experiments on a large scale include those on condensed phase explosives such TNT and other military explosives at the Aberdeen Proving Ground (W.E. Baker, 1973) and other military sites. Buildings and equipment have been subjected to condensed phase explosions in Nevada (Glasstone and Dolan, 1980). Large scale work on vapour cloud explosions has been done in the Netherlands (van Wingerden, 1989a).

In addition to the HSE laboratories just described other European centres include the Shell Thornton Research Centre (TRC) (D.C. Bull and Strachan (1992), the British Gas laboratories at Solihull, Loughborough and Killingworth and sites at Fauld and Spadeadam (Clerehugh, 1991), the Prinz Maurits Laboratory of TNO in the Netherlands (Groothuizen, 1988) and the Christian Michelsen Institute at Norway (CMI, 1992). UK centres specializing in fire include the Fire Research Station at Borehamwood and the Department of Fire Safety Engineering at Edinburgh University.

Work on disasters is undertaken in the UK at the Disaster Prevention and Limitation Unit at the University of Bradford (Keller and Wilson, 1991) and in the USA at the Disaster Research Center at the University of Delaware (Quantarelli, Dynes and Wenger, 1986). This is also the field covered by the Hazards Forum under the auspices of UK engineering institutions.

The European Community has had a wide-ranging programme of work on major hazards, particularly dense gas dispersion and vapour cloud explosions. This work is described by the Commission of the European Communities (CEC, 1989) and by Storey (1992). The commission maintains the Joint Research Centre (JRC) at Ispra, Italy, which includes the European Laboratory for Structural Assessment (ELSA).

The work of many of these research centres is described in other chapters, mainly in Chapters 15–17.

27 Information Feedback

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The feedback of information about incidents, accidents and failures, and about the performance of preventive measures, is a crucial aspect of the management system.

Some aspects of information feedback are considered here. Others are dealt with in other chapters, in particular Chapters 6, 8, 21 and 28.

Selected references on information feedback are given in Table 27.1.

Table 27.1 *Selected references on information feedback (see also Tables 1.1, 6.1 and 28.1)*

Guelich (1956); Heinrich (1959); Simonds and Grimaldi (1963); ABCM (1964/3); H.H. Fawcett and Wood (1965, 1982); McElroy (1965); Gilmore (1967, 1970); BCISC (1969/9); Handley (1969, 1977); Arscott (1975); Byrne (1975); Hearfield (1975); Kletz (1975a, 1976a, 1979c,h); Wellman (1975); Dawes and Davies (1977); Pitts and Gowan (1977); R.W. Henry (1979); NFPA (1990 NFPA 901, 902M); Hancock (1992 LPB 105)

Incident reporting, total loss control
BSC (n.d./6, 7); NRC (Appendix 28 *Incident Reporting*); Heinrich (1959); Bird and Germain (1966); J.A. Fletcher and Douglas (1971); Webster (1974, 1976); Dukes (1975); Hearfield (1975); Laitinen (1982); Lewis (1989 LPB 87); I.D. Brown (1990a); HSE (1992b); Brazier (1994)

Incident investigation and analysis
NRC (Appendix 28 *Incident Investigation*); SMRE (*Incident Investigation* 1); Guelich (1956); ABCM (1964/3); Bulkley (1967); Lynch (1967, 1973); Spiegelman (1969); Webb (1969); Siebert (1970); Houston (1971); W.G. Johnson (1973a,b, 1975, 1977, 1980); Benner (1975a); D.G. King (1975); R.J. Parker (1975); A.R. Baker (1976); Gugan (1976); Strehlow and Baker (1976); W.E. Baker, Westine and Cox (1977); R. King and Taylor (1977); Nertney (1976, 1978); Leplat (1978a); Bruun, Taylor and Rasmussen (1979); Beyers (1980); Robinson (1980 LPB 33); Ursenbach (1980, 1983); Burgoyne (1981/82, 1982); Sheehy (1981); Kletz (1979g,h, 1982a,b, 1983a, 1984a, 1986a, 1988h); HSE (1980 EM1, EM3); W.E. Baker (1982); Feggetter (1982); Pimble and O'Toole (1982); Searson (1982); Wiestling (1982); Zilka (1982); Boissieras (1983); Kjellen (1983); Mollerhoj and Robert (1983); van der Schaaf and Steunenberg (1983); Suokas and Rouhiainen (1984); Benner (1985); Vaija, Jarvelainen and Dohnal (1985, 1986a); Anon. (1986 LPB 72, p. 21); S.J. Brown (1987); Duguid (1987); Hendrick and Benner (1987 ACGIH/14); Leplat (1987); Suokas (1987); Ferry (1988); Mosleh *et al.* (1988); van der Schaaf (1988); I.D. Brown (1990a); Dowell (1990); ILCI (1990); S.E. Anderson and Skloss (1991); Svenson (1991a,b); Livingston and Green (1992); Philley (1992b); Nishikawa (1993)
Fire, explosion investigation : FPA (CFSD AR series, AR 1, AR 5); J. Kennedy (1962); Huron (1963); Bulkley (1967); Kirk (1969); W.B. Howard (1972); Sadée (1973a); R.J. Parker (1975); V.J. Clancey (1972b, 1981); Anon. (1975 LPB 2, p. 15); A.R. Baker (1976); FRS (1976 Fire Res. Note 1054); Guenther *et al.* (1976); Gugan (1976); Levinson (1977); Ettling (1978); Guenther, Goodwin and Brininger (1978); Dennett (1980); Yallop (1980); Beland (1981, 1982); Craven (1981, 1982); McIntyre (1981); Willis (1981); W.E. Baker (1982); Delplace and Vos (1983); D.A. Gray, Drysdale and Lewis (1983); R.J. Harris (1983); G.D. Davis (1987); Zeeuwen (1988); Cullen (1990); Taillet (1991); I.F. Thomas (1993, 1995); I.F. Thomas and Gugan (1993)
Transport investigations: NTSB (annual reports); Lasseigne (1984)

Warnings, near misses
NRC (Appendix 28); Pitts and Gowan (1977); Laitinen (1982, 1984); Lees (1982b, 1983b, 1985); N. Carter and Menckel (1985); Anon. (1989 LPB 85, p. 7); van Hemel, Connelly and Haas (1990); A.R. Hale *et al.* (1991); Ives (1991); D.A. Lucas (1991); Reason (1991); van der Schaaf, Lucas and Hale (1991); van der Schaaf (1991a–c)

Safety effectiveness, safety measurement
HSE (OP 9, 1986 PML 10, 1992 *Oil Industry* 3); Wynn (1950); Grimaldi (1960, 1965, 1970); Pollina (1962); Tarrants (1965, 1970, 1973); Rockwell and Bhise (1970); Anon. (1975 LPB 2, p. 12); Hooper (1975); S. Dawson, Poynter and Stevens (1982); Pastorini *et al.* (1986); Kaufman (1988); Gruhn (1993); Marcombe, Krause and Finley (1993)

Governmental investigation, disaster inquiries
Mecklenburgh (1977a); Davidson (1984); Crossland (1991); Fennell (1991); Wells (1991); I.F. Thomas (1993); I.F. Thomas and Gugan (1993); Lees (1994b)

Particular inquiries (see also Appendices 1–3, 5, 6, 16, 19, 21, 22)
R.J. Adams (1967); H. Griffiths, Pugsley and Saunders (1968); F. Morton (1970); Merrison (1971); R.J. Parker (1975); Ministry of Social Affairs (1976); Orsini (1977, 1980); Gjerde (1977–78); Costello (1979); Shooter (1980); Naesheim (1981); Hickman (1984); Layfield (1987); Sheen (1987); Steel (1987); Fennell (1988); O'Riordan, Kemp and Purdue (1988); Hidden (1989); Barnes (1990); Cullen (1990); Donaldson (1994)

Information retrieval, organizational memory
Kletz (1980g, 1982j, 1993c); A.F. Roberts (1980); R.W. Fawcett and Kletz (1982); Hancock (1989, 1992); K. Rasmussen and Gow (1992)

Information exchange, publication
Kletz (1985g,q); Resen (1985b); Glass and Rivard (1987)

HSE information services, HSELINE
Pantry (1986, 1987 LPB 78); HSE (1990 HSEL 1); Lewis (1993 LPB 114)

Education
Imperial College (1975); Butler, Ball and Pearson (1978); Beveridge (1979 LPB 27); Lees (1980b); Lihou (1981 LPB 40); D.B. Nelson (1982); HSC (1983); Mewis (1984); Anon. (1985f); Anon. (1985 LPB 62, p. 13); Talty (1986); Kaufman (1987); Kletz (1988l, 1990a); Levitzky (1988); Crowl and Louvar (1989); Nolan (1989); Crawley (1991 LPB 102); V.C. Marshall (1991c); Pitt *et al.* (1991); Crawley and Scott (1992); Hazards Forum (1992); Lemkowitz (1992a,b); R.B. Ward (1993b,c); Louvar and Kubias (1994)
CCPS: Anon. (1986c)
IChemE: Anon. (1988i,j,q)

27.1 The Learning Process

It is clearly essential that the industry should learn from its mistakes so that as far as possible it avoids repeating them.

This need to learn has long been recognized and is dealt with by a system of accident reporting and investigation. On the basis of this information accident statistics are compiled and an attempt is made to determine the trend in safety performance. Case histories are obtained and general lessons are derived. These lessons give rise to changes of practice, which are often embodied in standards and codes of practice or training programmes. These results are then publicized.

This system is essentially similar at company and at national level. There are statutory requirements for the reporting and investigation of accidents. Company requirements may be confined to these or may include other incidents. Accident statistics, safety performance trends and case histories are produced, changes in practice are made and publicity is given to these at both company and national level.

The effectiveness of this approach depends very much on the way in which it is implemented. There are wide differences, for example, in the quality of incident investigation and consequently in the benefit derived from it. There is also considerable variation in the extent to which the real lessons of case histories are appreciated and applied.

There are also other weaknesses in most systems for learning from incidents. One of the most fundamental has to do with the nature of the accident process itself. An accident normally occurs only when a number of conditions are fulfilled. If some of these conditions are not met, there may be instead an incident or 'near miss'. In general, the ratio of near misses to accidents is several orders of magnitude. This is seen most clearly in civil aviation, which is one of the few fields where there is a requirement to report near misses. Thus in effect a system based on reporting only of accidents reduces drastically the amount of information from which learning can take place.

The recognition of this fact is the basis of the total loss control approach, as described in Chapter 1. With total loss control there is a requirement for the reporting not only of personal injury but also of property damage accidents.

Not all near misses, however, result in property damage. Another important category of near misses is the operational incident. The aircraft near misses just mentioned are in fact mainly incidents associated with excursions outside operational limits rather than with damage to equipment. The chemical industry, however, does not appear to have a mechanism for learning from operational near misses.

Another weakness of the usual approach to learning stems from the nature of the hazards on process plants. It is a characteristic of complex technological systems that they allow very little scope for learning gradually by trial and error. Instead it is necessary to try to eliminate failures from the start.

This is the reason for the growth in reliability engineering and it has implications for the learning process. It means that attention needs to be concentrated not only on the accidents but also on the failures within the system which in a proportion of cases result in an accident. The emphasis on learning shifts then to the assessment of system reliability and to the collection of data required on equipment failure and human error.

It is not enough, however, to discover the facts about accidents. It is even more necessary to make sure this information is used. A high proportion of accidents constitutes repetitions, with only minor variations, of accidents which have already occurred elsewhere and which are well understood by the engineering profession as a whole. It is not to be expected that the individual engineer should familiarize himself with all these. But he should make it his business to become familiar with some of the exemplary case histories and their lessons. In addition, he should make use of aids such as checklists and codes of practice which embody much of this experience in the most readily usable form.

If learning is to take place, therefore, it is necessary to have both a means of obtaining information, e.g. accident reporting and investigation, and a means of ensuring that this information is utilized, e.g. checklists and codes of practice. It is desirable for the learning process to take place at both company and national level and the measures described are therefore necessary at both levels.

27.2 Incident Reporting

A system for reporting accidents and perhaps other incidents is necessary at company level. The minimum system is one limited to meeting the requirements for statutory reporting of accidents.

The national reporting requirements, which are described in Chapter 3, have been extended in recent years to cover certain types of event not previously included, such as leaks.

Such statutory requirements, however, are intended to assist the national learning process. The real object of a company reporting system should be to help the company to learn. It may be appropriate, therefore, for there to be a requirement for the reporting of additional types of incident. Events likely to be of particular interest in safety and loss prevention include:

(1) leaks of flammable materials;
(2) leaks of toxic materials;
(3) leaks and/or fires at pumps;
(4) fires/explosions on burners;
(5) storage tank collapse;
(6) malfunctions of pressure systems items (relief valves, non-return valves, vents);
(7) incidents involving trip system malfunction or disarming;
(8) incidents involving alleged operator error.

It is necessary to define carefully the level of incident which is reportable. This can be done satisfactorily at company level so that the reporting is adapted to the particular circumstances and produces useful information.

A reporting system is not of much value unless the information which it generates is utilized.

It is also appropriate here to refer again to total loss control, which involves a system both of incident reporting and of subsequent action, although in this case the emphasis is on some form of damage.

27.3 Operations Monitoring

In addition to incidents which have some physical result, such as the leakage of flammable materials or the collapse of a storage tank, there are also other incidents, such as excursions outside the specified operating conditions. These operational incidents also may constitute near misses.

The monitoring of operations from this viewpoint, however, is not well developed. The instrumentation provides trend records of selected variables and the operator records certain types of incident or excursion. These may be analysed or discussed with him by the plant manager. With the advent of process computers there is also a record of the alarm excursions of a larger number of measurements and of the operator's interventions via the computer. This information is mainly used in *ad hoc* investigations.

The Court of Inquiry on the Flixborough disaster experienced some difficulty in extracting useful information from the process instrumentation, most of which was destroyed by the explosion and the collapse of the control room. The report (R.J. Parker, 1975) suggested, therefore, that consideration should be given to the creation of a statutory requirement for the installation on such plants of a 'black box' facility such as is carried on aircraft.

This facility in aircraft is governed in the UK by the Air Navigation Order 1972, Schedule 5, which requires that certain aircraft, essentially those involved in public transport, should be equipped with a flight data and cockpit voice recording system approved by the Civil Aviation Authority (CAA). A flight data recorder system is required which records a list of specified parameters (e.g. pressure, altitude, airspeed, compass heading, pitch and roll attitudes) with a specified logging interval, accuracy and reliability. A crash-protected recorder is also required which will retain a record of these parameters in the event of aircraft crash. This is the so-called 'black box', although it is actually more like a red football in appearance. As already mentioned, a cockpit voice recorder is also a requirement.

This system therefore gives a complete record of the flight, including the information on maloperations and near misses, the number of which exceed actual crashes by several orders of magnitude.

The information given by the cockpit voice recorder is very useful and in crash investigations can be as important as the instrument data.

It will be apparent that the aircraft black box is in effect a system rather than a piece of hardware. It works well for aircraft where the parameters which should be specified for recording are standard, where the correct flying behaviour is well defined, and where there is a single authority which can analyse the data. Its application to chemical plant is more open to question for several reasons. Chemical plants already have a considerable amount of recording, particularly those with computers. There is much greater variation in chemical plants, both in the instrumentation and in the operation. Any analysis of the operations recorded would almost certainly be practical only at company level. Furthermore, despite Flixborough, it is not very often that the process instrumentation is destroyed.

If the object is to further the learning process at national level, it would seem more profitable to concentrate attention on a more systematic approach to the analysis of process operations in order to learn about near misses rather than to provide protected recorders which are used only to assist rare Courts of Inquiry. There would seem to be considerable scope for the operations monitoring of process plants. This might be somewhat on the lines of the replay of the aircraft flight data record, but as always any system used would have to be adapted to the rather different characteristics of chemical plants.

Nevertheless, the provision of a facility akin to the aircraft black box system is quite practical on chemical plant, particularly where there is a process computer. The main requirements for such a system are the provision of a schedule of data to be recorded, the proper maintenance of the instruments and the protection of the system against fire/explosion.

27.4 Accident Models

Accident models, which have already been considered in Chapters 2, 8 and 26, are here considered again briefly from the viewpoint of accident investigation.

Not all accident investigators find it helpful to make use of an accident model, but some do. Work on accident models for use as aids in accident investigation has been described by Benner (1985) and the Center for Chemical Process Safety (CCPS) (1992/1).

27.4.1 Logic tree models

Perhaps the most widely used form of accident model is the logic tree, this term being taken here to cover fault trees and other methods with a tree structure.

The Management Oversight and Risk Tree (MORT) of W.G. Johnson (1980), described in Chapter 2, provides a methodology for either investigating an accident or assessing a situation. MORT gives an idealized safety system represented as a logic tree containing specific control factors and general management factors. There is a text commentary which helps to identify good and bad practice.

Another logic tree method, the causal tree, derives the work of Leplat (1978a, 1987). This model resembles a fault tree, but is applied to an event which has already happened and which therefore contains no OR gates, only AND gates. Construction of the tree is guided by simple rules which specify the event chains. The aim of the method is to identify those changes which can be made to break the chain of events.

27.4.2 STEP

A model which does not have a tree structure is the Sequentially Timed Events Plotting (STEP) procedure of Hendrick and Benner (1987 ACGIH/14). The elements of the model are actors, actions and events. An actor can be a person, equipment, substance, etc., whilst an action is anything brought about by an actor, and an event is the unique combination of an actor and one action. A structured procedure is used to create a model of the accident from these elements.

27.4.3 Kletz model

Kletz states that he does not find the use of accident models particularly helpful, but does utilize an accident causation chain in which the accident is placed at the top and the sequence of events leading to it is developed beneath it. An example of one of his accident chains is given in Chapter 2. He assigns each event to one of three layers:

(1) immediate technical recommendations;
(2) avoiding the hazard;
(3) improving the management system.

In the chain diagram the events assigned to one of these layers may come at any point and may be interleaved with events assigned to the other two layers.

It is interesting to note here the second layer, avoidance of the hazard. This is a feature which in other treatments of accident investigation often does not receive the attention which it deserves, but it is in keeping with Kletz's general emphasis on the elimination of hazards and on inherently safer design.

27.4.4 Comparative studies

A comparative study of the characteristics of three accident models as applied to accident investigation has been made by Livingstone and Green (1992). They start from the perspective that investigations are generally too biased towards technical factors and take insufficient account of root causes. They identify three accident models as potentially useful: the causal tree model, MORT and STEP.

Livingstone and Green find that the causal tree method provides little guidance on how to collect the relevant information or identify the main events involved. It deals mainly with the direct causes, or trigger events, and does not deal so well with the root causes. They view STEP as well structured, but again as being of little assistance with root causes. They see MORT, on the other hand, as excelling in the identification of root causes, but as requiring the accident sequence to be identified separately.

These authors propose a hybrid model which combines STEP and root cause analysis.

27.5 Accident Investigation

Accident investigation is described in *Professional Accident Investigation* (Kuhlman, n.d.), *Modern Accident Investigation and Analysis* (Ferry 1988), *Learning from Accidents* (Kletz 1988h, 1994) and *Forensic Engineering* (Carper, 1989) and by Bulkley (1967), M.E. Lynch (1973), Kletz (1979g, 1984a), Burgoyne (1981/82, 1982) and Craven (1982).

Some accounts of accident investigation are concerned essentially with in-house investigations, whilst others describe the viewpoint of the consultant investigator. The account given here starts with a consideration of the selection of the investigator, either in-house or a consultant. It continues with a review of the purposes of investigation from the perspective of a consultant and then with the organization and conduct of an investigation, basically the technical aspects, again written from the viewpoint of a consultant, although the principles are equally applicable to an in-house investigation. Next, consideration is given to some particular types of investigation. The account then considers the investigation of the deeper causes of the accident and the recommendations for prevention, written largely from the viewpoint of the in-house investigator. The section concludes by considering a number of other topics related to investigations.

27.5.1 Selection of investigator

A formal system for the appointment of an accident investigator should be part of the emergency planning in a company. The selection of an investigator is discussed by Craven (1982). The choice is of particular importance if the accident is a major disaster. In this case it will usually be necessary to appoint a multi-disciplinary team, but the team will still require a leader. Craven considers the selection of the investigator under two headings: expertise and affiliation. Professional expertise and qualifications are factors to be taken into account, but personality and investigatory experience are also important. For small accidents an in-house investigator may often be appropriate, but for a large accident it may be preferable to call in an outsider who is free of company involvement and is perceived as more independent.

27.5.2 Purpose of investigation

The usual purpose of an investigation is to determine the cause of the accident and to make recommendations to prevent its recurrence. There may, however, be other aims, such as to check whether the law, criminal or civil, has been complied with or to determine questions of insurance liability.

The situation commonly faced by an outside consultant is described by Burgoyne (1982) in the following terms:

> The ostensible purpose of the investigation of an accident is usually to establish the circumstances that led to its occurrence – in a word, the cause. Presumably, the object implied is to avoid its recurrence. In practice, an investigator is often diverted or distorted to serve other ends. This occurs, for example, when it is sought to blame or to exonerate certain people or things – as is very frequently the case. This is almost certain to lead to bias, because only those aspects are investigated that are likely to strengthen or to defend a position taken up in advance of any evidence. This surely represents the very antithesis of true investigation . . .
> Ideally, the investigation of an accident should be undertaken like a research project.

It is, however, relatively rare for such investigations to be conducted in this spirit.

27.5.3 Organization of investigation

Often there will be separate investigations carried out by the company and by the regulatory body, which in the UK is the Health and Safety Executive (HSE). It is important, therefore, that the responsibilities of the investigation teams and of the individual investigators be clearly defined, and that people who may be affected by their activities be informed.

The investigation should start as soon as possible after the incident, while memories are still fresh and evidence is undisturbed. In particular, photographs, measurements and similar evidence should be taken on the site as early as possible.

The precise procedure for an investigation cannot be rigidly defined in advance. It may involve assessment of damage and interviewing of personnel and may include laboratory work such as metallurgical examination and simulation work such as the operation of equipment under simulated process conditions.

27.5.4 Conduct of investigation

The form taken by an investigation depends somewhat on the accident, but is likely to be broadly as follows: (1) remit, (2) preliminary site visit, (3) collection of background information, (4) examination of damage, (5) interviewing of witnesses, (6) research and analysis, and (7) final report.

The purpose of the investigation should be clearly defined from the outset and a clear remit obtained. If in the course of the investigation it proves to be necessary, the remit should be renegotiated. The investigator should also ascertain the general circumstances of the accident.

The preliminary site visit should be made as soon as possible. The first matter to be considered is the potential hazards. The situation pertaining after a large accident particularly is, in the nature of the case, an uncontrolled one. Some of the hazards enumerated by Burgoyne (1982) are: mechanical hazards, such as falling through collapsing structures or due to unsafe access, falling objects such as lifting gear, striking and crushing by collapsing structures, and collision with dangerous objects; thermal hazards of hot surfaces and fluids, and concealed fires; chemical hazards from corrosive, flammable or toxic materials, present as spills or in confined spaces or giving rise to sprays; and electrical hazards from live circuits and equipment.

At this stage the site should not be disturbed. Photographs of the site are, however, invaluable. Colour photographs are preferred, since they give much more information, particularly on fire damage. A record should be kept of the location and viewpoint of each photograph. Sketch plans, sketches and notes should be made as appropriate. It may be helpful to obtain an overview of the site by viewing it from a distance, perhaps from the window of a nearby building.

During this visit the names should be obtained of eyewitnesses and of others who may have relevant information. Witnesses should be encouraged to write down their experience whilst it is fresh and, if possible, before they have talked to other witnesses.

The investigator needs to familiarize himself with the details both of the process and of the plant equipment.

Examination of the damage caused by the accident usually yields much useful information. Some of the detailed features of fire and explosion damage are considered below.

The interviewing of witnesses is another important source of information but requires some care. Information should be sought on the situation immediately before as well as during and after the event. Allowance needs to be made for the fact that the account given by a witness may be defective by reason of the initial observation, memory or descriptive powers. Accounts of sudden, short and violent events in particular tend to be unreliable. The interviewer should avoid the use of leading questions and should seek to cross-check accounts given.

There follows a period of analysis and research. The danger of jumping to a conclusion and the need to keep an open mind are often emphasized. Burgoyne argues that the use of a working hypothesis, possibly with variants, is necessary, provided it continues to be treated as no more than that. The working hypothesis is then tested and adjusted, typically by an iterative process.

There may be some issues which can be resolved only by physical tests. In some cases small scale tests are adequate, but frequently the only tests capable of providing results which will carry conviction are relatively large scale, time-consuming and expensive. One reason for the time and expense may well be the hazards of the work required. The decision as to whether to call for tests is often one of the most difficult which an investigator has to take.

There comes a point where further work is subject to the law of diminishing returns and the investigator has to come to a conclusion, even if, as is usually the case, there are loose ends.

A report is then written. This may well be best cast in the form of a chronological account of the steps by which the investigator came to his conclusion. The elements of an accident report are described by Craven.

27.5.5 Findings of investigation

An investigation is expected (1) to determine what happened and why it happened and (2) to propose how it might be prevented from happening again. These two outcomes constitute the findings and the recommendations of the investigation.

It is common for reports of accident investigations to draw conclusions, and make recommendations, which are concerned almost entirely with technical matters, and which fail to delve deeper into the more fundamental causes.

This characteristic of the conclusions of an accident inquiry is often virtually guaranteed by the way the investigator is chosen. Management assumes that the causes are technical and appoints to investigate them the person who seems to have the best technical qualifications for the task. He in turn assumes that he has been appointed to discover the technical cause(s).

In fact accidents are typically the result of a combination of failures, technical and human, both of which are outcomes of management failure. Various aspects of this have been described elsewhere, notably in Chapters 2, 6, 9 and 14.

This characteristic of accidents is now common ground in the literature on accidents and their investigation. Different aspects are emphasized by different authors. For example, Reason (1991) stresses the prior presence of latent failures, or resident pathogens; Swain (1972) emphasizes the work situation and the associated performance shaping factors; and Bellamy (1984) stresses communication failures.

The need for a 'layered' accident investigation which strips off the surface layers and delves down to these deeper causes is a persistent theme in the work of Kletz on accident investigation and of learning from accidents; he calls it 'peeling the onion'. Some authors use an accident model and/or taxonomies of causes as an aid to laying bare the structure of the accident.

The basic message of such work is that, at the end of the day, it is management which has the responsibility of

ensuring that the deficiencies and failures of equipment and humans are so controlled that accidents are avoided and that recommendations for preventing a recurrence must start from this perspective.

However, the proposition that accidents are always in some sense attributable to management is not in itself especially constructive. It is much more helpful to identify the particular failings which repeatedly contribute to accidents.

Most workers on accident investigation give their own classifications of these failings. For example, the classification given by Reason in relation to near misses is quoted in Section 27.16.

Another classification is that of Kletz, which, as already mentioned, treats the accident in terms of the three layers (1) immediate technical recommendations, (2) avoiding the hazard and (3) improving the management system.

Kletz makes a number of suggestions for things to avoid in accident findings. It is not helpful to list 'causes' about which management can do very little. Cases in point are ignition sources and 'human error'. The investigator should generally avoid attributing the accident to a single cause. Kletz quotes the comment of Doyle that for every complex problem there is at least one simple, plausible, wrong solution.

Increasingly, the findings of accident investigations are presented in terms of the root causes. The concept of root causes has been discussed in Chapter 8 and is considered further in Section 27.8. It underlies the family of techniques described by Wells and co-workers, the audit methodology being developed by the HSE and the approach suggested by the CCPS. The findings should identify the specific root causes and the recommendations should then address each of these in turn.

27.5.6 Recommendations of investigation

As just indicated, the recommendations should arise out of the findings of the investigation. The investigation should aim to match each root cause with a corresponding appropriate recommendation.

A recommendation will generally address one of three aspects of the accident situation: (1) reduction of frequency, (2) reduction/mitigation of consequences and (3) limitation of exposure of people.

In terms of the fault tree representation, the aim is to insert a new, or to strengthen an existing, AND gate at each critical point in order to prevent escalation up the demand tree.

It is urged by Kletz that technical proposals for prevention should aim for defence in depth and therefore should give due weight to the earlier as well as the later lines of defence. In fault tree terms, there should not be excessive concentration on the upper levels of the tree just below the top event.

Lines of defence which Kletz lists, some applicable only to flammables, are (1) limitation of inventory, (2) inspection of construction, (3) gas detectors, (4) leak warning system, (5) leak isolation, (6) leak dispersion by open construction and fluid curtains, (7) elimination of ignition sources, (8) passive fire and explosion protection, (9) active fire fighting measures and (10) separation distances.

Kletz identifies as recurring themes in general recommendations in his own analyses of accidents (1) design of user-friendly plants, (2) hazard identification by hazard and operability (hazop) studies, (3) control of plant modification and (4) inspection and testing of protective equipment.

Another recurring theme is management, which has a number of aspects, including (1) organizational memory and (2) training.

Recommendations may seek to exploit the concept of hazard warning outlined in Chapter 9. From this viewpoint, the existence, or insertion, of an AND gate in the fault tree means that the events below that gate, if observable, may be monitored and treated as warnings.

It is good practice to draw up draft recommendations and to consult on these before final issue with interested parties. This contributes greatly to their credibility and acceptance.

It is relevant to note that in a public accident inquiry such as the Piper Alpha Inquiry the evidence, both on managerial and technical matters, on which recommendations are based is subject to cross-examination.

The recommendations should avoid over-reaction and should be balanced. It is not uncommon that an accident report gives a long list of recommendations, without assigning to these any particular priority. It is more helpful to management to give some idea of the relative importance. The *King's Cross Report* (Fennell, 1988) is exemplary in this regard, classifying its 157 recommendations as (1) most important, (2) important, (3) necessary and (4) suggested.

In some instances plant may be shut down pending the outcome of the investigation. Where this is the case, one important set of recommendations comprises those relating to the pre-conditions to be met before restart is permitted. These recommendations may well involve process and/or plant modifications and, if so, should be subject to the established systems for management of change.

There should be full documentation of the recommendations, covering those considered and rejected as well as those accepted.

27.5.7 Report of investigation

The investigation is documented in the final report. If it is a lengthy one, it may also be appropriate to issue an interim report.

The final report should include: an executive summary; an outline of the accident; a statement of the scope of the inquiry; the background, which will often need to cover relevant aspects of the management systems, the process, the plant and its operational history; a narrative of the events prior to and comprising the accident; an account of the investigation itself; a listing of the findings, with supporting evidence; and a listing of the recommendations, with clear links to the findings.

The requirements for follow-up of the report should also be specified in writing, whether in the report itself or otherwise. These include dissemination of the report's contents and action on it recommendations.

27.5.8. Experimental work

It is necessary in some investigations to undertake experimental work. Two main types of investigation are tests on failed equipment and experiments undertaken to test a hypothesis.

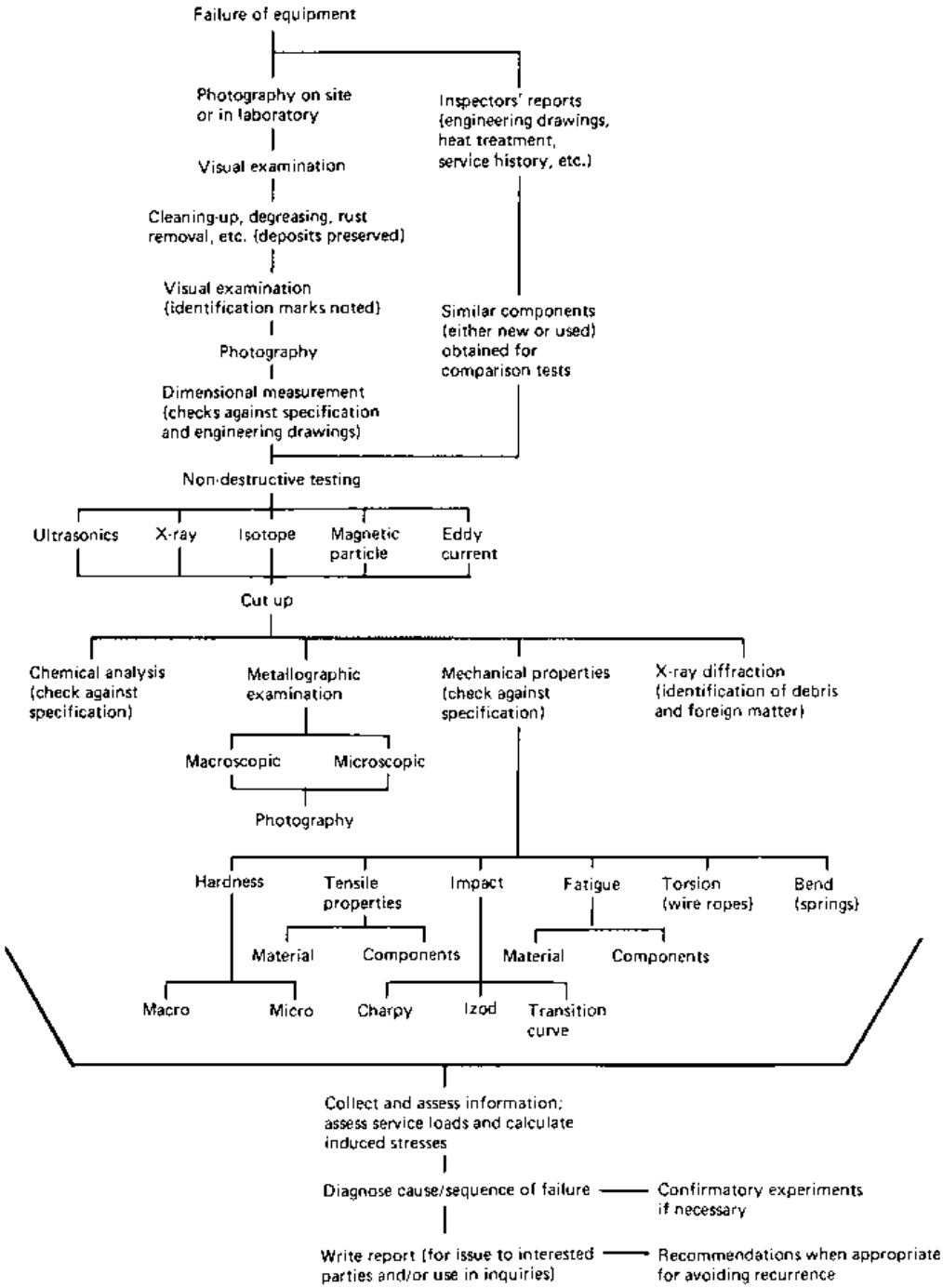

Figure 27.1 *Sequence of events in the examination of faulty equipment (Safety in Mines Research Establishment, 1971, Engineering and Metallurgy 4; reproduced by permission. The sequence may be modified and stages omitted according to the type of failure)*

The damage survey in the field is often complemented by laboratory examination of failed equipment. Figure 27.1 illustrates the procedure used at the time for examination of equipment failure by the Safety in Mines Research Establishment (SMRE), an HSE 'in-house' facility. Some of the inspection techniques have been described in Chapter 19.

An account of the approach taken in experimentation done to test a hypothesis is given by A.R. Baker (1982). Simulation experiments are done for three basic purposes: (1) to confirm or demonstrate, (2) to identify a mechanism, or (3) to determine an initial condition. Thus an experiment may be carried out to confirm or demonstrate convincingly that a particular event or sequence of events could have occurred under appropriate conditions. The relevance of such work depends on the extent to which the conditions of the accident can be simulated. Failure to reproduce even one of these initial conditions to which the results are known, or expected, to be sensitive may vitiate the work. In other causes the initial conditions and the results are known, but the mechanism is not understood. There may be several candidate mechanisms. In yet other cases the aim is to determine the initial condition(s) which caused the event of interest. Where there is a sequence of events, it is often impractical, and unnecessary, to simulate the whole sequence; it may be sufficient to simulate just one of these events.

It is generally easier to show that something could happen than that it could not. For the former a single positive result suffices, whereas for the latter the experimental space to be explored may be very large.

In many cases a small scale experiment is not adequate, but large scale experimentation may be problematic, and is often potentially hazardous. It is likely to be expensive and time-consuming.

Where experiments are carried out, it is good practice to make a full photographic record.

Baker describes some seven different experimental investigations, including work on the bellows assembly at Flixborough and on a gas explosion in a building.

27.5.9 Some types of investigation

The account given so far has considered accident investigations conducted either in-house or by a consultant investigator. As mentioned earlier, accident investigations may also be carried out to check compliance with the law or to determine insurance liability. Where a crime is suspected, the police will be involved and may draw on resources such as those of the Home Office Forensic Science Laboratories. Where a violation of health and safety legislation is at issue, the HSE will be involved and may choose to conduct their own investigation, as described below. Where there is a question of the applicability of an insurance policy or the possibility of a transfer of liability to another party, one or more of the parties concerned may conduct their own investigations. It can occur, therefore, that there is more than one investigation of the accident going on at the same time.

27.5.10 Regulatory investigations

In the UK, a proportion of the more serious accidents are investigated by the HSE. It is the normal practice to publish the report. HSE reports in the *Investigation Report* series, listed in Appendix 28, include the following: *Explosion at Laporte Industries, Ilford, 5 April 1975* (HSE, 1976b), *Explosion at Appleby Frodingham Steelworks Scunthorpe, 4 November 1975* (HSE, 1976a), *Explosion at Dow Chemical Factory, King's Lynn, 27 June 1976* (HSE, 1977b), *Fire and Explosion at Braehead Container Depot, Renfrew, 4 January 1977* (HSE, 1979b), *Leakage of propane at Whitefriars Glass Limited, Wealdstone, Middlesex, 20 November 1980* (HSE, 1981c), *Fire and Explosions at B&R Hauliers, Salford, 25 September 1982* (HSE, 1983b), *Abbeystead Explosion, 23 May 1984* (HSE, 1985a), *Summit Tunnel Fire* (HSE, 1985e), *The Fires and Explosion at BP Oil (Grangemouth) Refinery Ltd, 13 March, 22 March and 11 June 1987* (HSE, 1989a) and *The Peterborough Explosion of a Vehicle Carrying Explosives, 22 March 1989* (HSE, 1990b).

Likewise, in the USA if an accident is sufficiently serious an investigation is conducted by the Occupational Safety and Health Administration (OSHA). The report *Phillips 66 Company Houston Chemical Complex Explosion and Fire* (OSHA, 1990a) is a case in point.

Investigations into transport accidents in the USA are conducted by the National Transportation Safety Board (NTSB). Some of their reports are listed in Appendix 28.

27.5.11 Public inquiry investigations

The *Flixborough Report* (R.J. Parker, 1975) together with its associated daily transcripts and the documents submitted to the inquiry remains perhaps the most comprehensive account of an accident investigation in the chemical industry. References to some of the large number of reports are given in Table A2.1. Accounts by individual investigators include those by Tucker (1975), J.I. Cox (1976b) and Gugan (1976). Further details of the Flixborough investigation are given in Appendix 2.

The *Piper Alpha Report* (Cullen, 1990), with its associated transcripts and the papers published subsequently, is another illustration of a major accident inquiry. References are given in Table A19.1. Accounts of individual investigators include those of Bakke (1989), R.A. Cox (1989a), M.E. Davies (1989), S.M. Richardson (1989) and Saville (1989). Further details of the Piper Alpha investigation are given in Appendix 19 and an account of the inquiry is given in Section 27.9.

27.5.12 Illustrative examples

There are available in the literature a large number of reports and other accounts of accident investigations which serve as illustrative examples. At the top level there are the reports of public inquiries such as the *Flixborough Report* and the *Piper Alpha Report*. At the next level down are the accident investigation reports of the HSE and the NTSB, to which reference has just been made.

The work of Kletz gives a large number of accounts of accidents, each with an analysis which is an illustration of the principles of investigation which he advocates, together with explicit statements of those principles.

An account is now given of two further illustrative examples of the techniques of accident investigation.

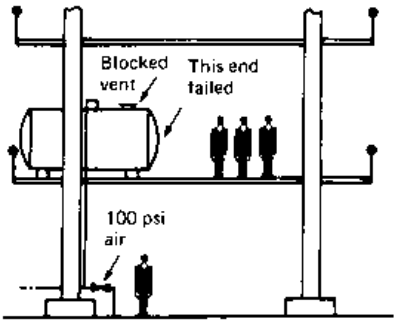

Figure 27.2 *Accident involving the failure of a storage vessel (Houston, 1971) (Courtesy of the Institution of Chemical Engineers)*

27.5.13 Illustrative example: choked vent

An account of the investigation of accidents in process plants has been given by Houston (1971). This work was referred to earlier in Chapter 2. The approach taken is illustrated by an example which he gives of a hypothetical accident (see Figure 27.2):

> One end of a storage drum was blown out seriously injuring three men who were working nearby.
>
> The drum was used to store an organic liquid with a relatively high melting point. Steam tracing on the feed line was not very effective and chokes were common. Because of this it was customary to blow the line clear with air at 100 lb_f/in^2 before and after each transfer.
>
> On this occasion the operator realized that the vent was not blowing and assumed that the line was blocked. In fact it was the vent that was blocked and when the pressure reached an estimated 30 lb_f/in^2 one end of the vessel failed. Debris, particularly hot residual product from the last batch at 120°C, was blown some distance and three men who were working about 15 ft away were seriously injured.

The analysis of this accident using a model accident analysis form is shown in Table 27.2. The method has several important features. It does not report a principal cause, but rather a chain of events which might be broken in several places. It identifies both the advance warnings and the preventive measures that might be utilized to prevent recurrence, and it yields recommendations which are capable of practical implementation.

27.5.14 Illustrative example: ethylene oxide plant explosion

An illustration of the investigation of a quite different kind of accident is that undertaken following the explosion at the ethylene oxide/glycol plant of BASF on 7 March 1989 at Antwerp (Anon., 1991 LPB 100, p. 1). The incident involved an explosion on a distillation column separating ethylene oxide (EO) and acetaldehyde. The investigation found that probably a small leak of EO had led to an accumulation of auto-oxidizable polyethylene glycols in the insulation of the column.

The account referenced describes the organization of task forces to (1) secure the damaged plant, (2) repair the equipment, (3) document the damage, (4) assemble information, and (5) search for the cause.

A thorough review was made of the chemistry of the process and of the potential sources of ignition. The explosion event was reconstructed from an analysis of the damage, the examination of materials, the statements of eye-witnesses and the recorded information from nearby plants, and the probable chain of events leading up to the explosion reconstructed.

The location of the first explosion was identified as the acetaldehyde column K 303 from the fact that a manhole cover from this column had left an imprint on nearby column K205. The damage to the trays of the column indicated that the explosion occurred in the lower part of the column, probably at the bottom.

Alternative sources of ignition included chemical reaction of the bottom products, static electricity and EO decomposition in an overheated pump, but these were eliminated. The only ignition source which could not be discounted was a fire within the insulation. It was confirmed that this was a feasible mechanism. EO itself is a low boiling liquid which does not generally accumulate on insulation, but it reacts with water to give polyethylene glycol (PEG), a reaction which normally requires a temperature of 180°C but which was shown to proceed in direct contact with mineral wool at 100°C. The PEG is high boiling and can support self-heating of the insulation.

27.5.15 Disputed investigations

A large proportion of accidents are investigated by the fire services for the purpose of records and statistics, and the investigation is relatively short. Even where it is rather fuller, time and resource constraints still apply.

In some cases a later investigator comes to a different conclusion as to the technical causes. Three such cases are given by Ursenbach (1980, 1983). In the first the ignition of a vapour cloud from a plant leak was ascribed to a non-explosion-proof electric cart, but subsequent modelling of the vapour dispersion showed that a flammable mixture could not have reached the vehicle. In the second an explosion was attributed to a defective acetylene cylinder, but a later study of marks on the cylinder indicated that the damage to it had been caused by compression of an oxygen cylinder onto it by the collapsing roof. In the third case it was reported that the damage was due to an explosion of solvents evaporating from a massive ink spill caused by the failure of a ball mill at ground level, but a further investigation found that other explosions had occurred on upper floors which could not have been due to the heavier-than-air vapour on the ground floor.

27.6 Fire Investigation

Accounts of the investigation of fire are given in *Fire and Arson Investigation* (J. Kennedy, 1962) and *Fire Investigation* (Dennett, 1980) and by Burgoyne (1981/82, 1982) and Craven (1982).

The overall conduct of an investigation has been described above. The general account given of the preliminary site visit, the examination of damage, the interviewing of witnesses, etc., is applicable, but in

Table 27.2 *Model analysis of storage vessel accident (Houston, 1971) (Courtesy of the Institution of Chemical Engineers)*

	What was the immediate cause?	*What else made an accident possible?*	*What form of energy or poison was involved?*	*What was done to prevent an accident?*	*What was the point of no return?*	*What effect did the locality have?*	*What was done to reduce the severity?*	*Did the accident have any further repercussions?*
Please describe what happened	Turning on 100 $lb_f/in.^2$ air	Blocked 4 in. vent	40 m^3 of air at ~30 $lb_f/in.^2$ the calculated bursting pressure	Nothing	When vessel shell failed	Product at 120°C sprayed on three maintenance men who were 15 ft away across platform	Injured given first aid in control room. Fire and ambulance services called. Area washed down	Loss of this vessel restricted plant output for 3 months at cost of £18 000
Why did it happen?	To prove feed line was clear before transfer (history of blockages)	Product (m.pt = 105°C) sprayed on cold vent by air blowing. Vent not normally inspected (poor access)	50–100 $lb_f/in.^2$ needed to clear blocks ~30 $lb_f/in.^2$ could build up in tank in ~5 min	Operator knew vent was not blowing but assumed line was at fault (no PI or bursting disc provided)	Excess pressure designed only for 15 $lb_f/in.^2$	Tank had residue of product after transfer. Men on routine maintenance job	A/F and crew heard bang and came running	Delay caused by tank cleaning due to more frequent grade changes on other storage tank
Has this or anything similar happened before?	Daily for 8 years; also done on discharge line	Nothing proven. A tank was sucked in due to vent restriction 2 years ago – suspect that was lesson not properly learned	See safety adviser's file on overpressure incidents	Instructions do not call for vent inspection as blockage not anticipated	See safety adviser's file on overpressure incidents	Men must be in this area approximately 1% of time	–	No
What should be done to prevent a recurrence?	(1) Investigate use of internal steam tracing	(2) Provide heated 8 in. vent on replacement tank (3) Arrange for registration and routine inspection of all critical vents	(4) Write up piece on vents in next safety bulletin and discuss with training manager	Bursting disc not needed if vent modified (5) Draft works standing order on use of 100 $lb_f/in.^2$ air, etc., for line clearing	–	(6) Consult Engineering Dept on known modes of failure on location of access ways	–	–
MAIN RESULTS Men off 6, 9 and 30 days with burns Vessel destroyed – replacement cost £15 000 Product lost – 5 ton valued at £1500 Contingent loss £18 000				FOLLOW-UP 1 2 3 4 5 6	*Recommendation* Plant Engr Plant Engr Asst Wks Mgr Safety Adviser Asst Wks Mgr Safety Adviser	*Action*	*Completion*	

[a]A/F assistant foreman; PI, pressure indicator.

addition there are a number of considerations which apply specifically to fire investigation.

The preliminary site visit serves to identify the area of origin of the fire. Further work is aimed at establishing the material first ignited, the source of ignition and the general features and pattern of the fire and thus identifying the cause.

27.6.1 Fuel involved in fire

Some pointers to identifying the fuels involved in a fire or explosion are given by C.H.H. Willis (1981).

27.6.2 Temperature attained by fire

The temperature of a process plant fire does not normally rise much beyond 1000°C. This is so whether the material undergoing combustion is a flammable liquid or a solid material such as wood, plastic or paper. On the other hand it is usually sufficient to cause significant deterioration of steelwork, which occurs in the range 550°C to 600°C. Jet flames can give rise to temperatures appreciably higher than 1000°C.

Some indicators of the behaviour of the fire are charring of wood, melting of metals, damage to vessels and damage to structural steelwork. Charring of wood can be expected to be deepest where the fire has burned longest. Most types of wood are charred to a depth of about 2.5 cm within 40 minutes, whatever the fire, as long as the flame is the diffusion flame normal in a fire.

Copper has a melting point of 1080°C and usually does not melt but its alloys brass and bronze do, their melting points being in the range 800–1000°C. So does aluminium with a melting point of 650°C.

The paint on a vessel containing liquid may be blistered above the line of the liquid level but not below. If the original liquid level is known, this can be used in conjunction with an assumed heat input rate to estimate the duration of the fire. Craven suggests values for the heat input rate of 110 kW/m^2 typical and 170 kW/m^2 maximum, in the absence of a jet flame.

The temperature at which structural steelwork distorts is attained in most process plant fires, and the damage can be spectacular, but generally it is not a very helpful indicator.

Fire temperature indicators are also described by Guenther *et al.* (1976), Guenther, Goodwin and Brininger (1978) and McIntyre (1981). The latter gives an account of the use of common materials as temperature indicators. He divides such indicators into two classes: time independent and time dependent. Some indicators which are essentially independent of, or only weakly dependent on, time are the melting of metals, the charring of wood, the high temperature scaling of steel and the recrystallization of copper. He gives a list of some 25 temperature indicators which may be observed by one of three methods: visual examination, hardness testing or metallographic examination.

27.6.3 Electrical short circuits

Fires of electrical origin are of considerable interest to fire investigators. A relevant code is NFPA 907M.

Accounts of the treatment electrical short circuits in fire investigations are given by Levinson (1977), Ettling (1978), Beland (1981, 1982), Delplace and Vos (1983) and D.A. Gray, Drysdale and Lewis (1983).

An electrical short circuit is a potential source of ignition. It is accompanied by an electric arc. Such an arc causes damage to the electric wiring and leaves a visible mark. The problem is to determine whether in a given case the short circuit is a cause or an effect of the fire.

The differentiation of cause from effect is addressed by Delpace and Vos (1983) and experimental work to this end is described by D.A. Gray, Drysdale and Lewis (1983). Delplace and Vos also state that there is a close parallel between the pattern left by a fire and the location of the short circuits and that this can be exploited in fire investigation.

27.7 Explosion Investigation

Accounts of the investigation of explosions are given in *Unconfined Vapour Cloud Explosions* (Gugan, 1979), *Explosion Investigation* (Yallop, 1980) and *Investigation and Control of Gas Explosions in Buildings and Heating Plant* (R.J. Harris, 1983) and by V.J. Clancey (1972b, 1981), W.E. Baker (1982) and Craven (1982).

27.7.1 Types of explosion

There are a number of different types of explosion on process plant which the investigator may need to consider. They include:

(1) condensed phase explosion;
(2) physical explosion –
  (a) hydraulic,
  (b) pneumatic;
(3) confined gas explosion;
(4) vapour cloud explosion;
(5) boiling liquid expanding vapour explosion;
(6) dust explosion;

It may also be necessary to distinguish between deflagration and detonation.

Explosions may occur with buildings; gas explosions in buildings are of particular importance.

27.7.2 Condensed phase explosions

Explosions of a condensed phase explosive such as TNT are of less interest for process plant than are some of the other types, but on the other hand the methods of investigation are well established and accounts more comprehensive, so that it is convenient to start with them. Accounts include *Explosion Investigation* (Yallop, 1980) and that by V.J. Clancey (1972b). The effects of condensed phase explosions, which are well documented, are described in Chapter 17 and the information given there may be used for diagnostic purposes.

The text by Yallop covers (1) explosion accidents and the explosion investigator, (2) fundamentals of explosives, (3) the approach to the scene, (4) the observation and assessment of damage, (5) identification of the explosive, (6) causes of initiation, (7) explosions in moving vehicles, (8) injury to persons, (9) examination of suspects, (10) analysis of witness statements, (11) unlikely occurrences, (12) negative evidence and (13) drawing the conclusions.

Yallop's treatment of the observation and assessment of damage covers (1) the importance of damage, (2) the type of explosive and explosion damage, (3) the value to be attached to damage observations, (4) the importance

of the site of the explosion centre, (5) the determination of the site of the explosion centre, (6) the significance of pressure, (7) the application of pressure observations, (8) the phenomenon of fragmentation, (9) information from fragments, (10) craters, and (11) ground shock. Some of the relationships given by Yallop, and also by Clancey, are among those used in Chapter 17, which also draw on his accounts of explosives and of their initiation.

Observable damage falls into three categories: (1) permanent distortion of objects, (2) displacement of objects, and (3) flame and heat effects. Permanent distortion may itself be subdivided into (1) plastic deformation, (2) fracture, and (3) fragment attack. In general, permanently distorted objects are generally quite reliable indicators, whereas displaced objects are much less dependable.

Modes of plastic deformation considered include: (1) bending of long metal objects such as structural members, rails, window frames, pipes, and nails, screws and bolts; (2) dishing of metal plates, including tanks; and (3) movement of piles of particulate matter. The author states, however, that observations cannot be made on a container which is full of liquid, which inhibits distortion. Fracture may be observed of the structural elements of buildings, the contents of buildings, and objects outdoors. Fragment attack take the form of surface attack, giving dents or small craters, or penetrative attack. The latter can be useful in locating the explosion centre by projecting back the lines of the penetration holes.

Flame and heat effects are melting and decomposition. The contact between the hot gas of the blast wave and surrounding objects is generally too short for much heat transfer to occur, but metal surfaces close to the explosion centre can exhibit 'gas wash', which is characterized by partial melting of the surface layers, giving a ripple effect. In some cases heat transfer is sufficient to cause decomposition, such as the charring of organic materials or the discoloration of painted surfaces.

This information may be used to prepare a direction/damage diagram. Yallop describes a diagram made for the gas explosion in the flats at Ronan Point in 1968 with a detailed explanation of some 19 items.

The author gives a detailed account of the determination of overpressures from plastic deformation and from fractures. These may be used to determine the charge weight of the explosive using the usual scaling laws.

It is a basic principle of explosion investigation to recover as many primary fragments as possible. Fragments can give information on the nature of the exploding object and on the site of the explosion, and possibly the charge weight.

A further account is given by W.E. Baker (1982). He advises for the determination of explosion yield the use of the pressure–impulse method. He draws attention to the need to allow in the far field for meteorological effects due to possible focusing of inversions and wind shear.

27.7.3 Physical explosions

Physical explosions are often the result of overpressurization during a fire. Depending on whether the vessel is full of liquid or not, the explosion may be hydraulic or pneumatic. The mode of failure is determined by the weakest feature of the containment. A pneumatic explosion is the more violent and gives rise to a large number of missiles.

The estimation of the energy released in, and of the effects of, a physical explosion are described in Chapter 17.

27.7.4 Confined gas explosions

The behaviour of an explosion of gas confined within a plant depends on the nature of the space concerned. With a single volume such as a vessel the explosion can be expected to be a deflagration with a stress essentially uniform over the containment. With a multi-compartment volume there is scope for run-up to higher flame speed and for pressure piling. Damage is likely to be at a maximum at the point most remote from the source of ignition. With a pipeline the flame speed may accelerate to give a detonation.

Slow deflagration of a gas mixture tends to give a pure ductile failure at a pressure corresponding to the static strength of the container. The bursting of a cylindrical container in such a deflagration is usually taken to occur when the pressure causes the stress to exceed the hoop stress.

Where the flame speed in a gas mixture runs up to detonation, which can occur in a vessel of high aspect ratio or a pipeline, bursting may occur at a higher pressure than that for static loading. The bursting of a cylindrical containment in a detonation may be taken to occur at a pressure corresponding to a stress which is about twice the hoop stress.

Detonation in a pipeline gives rise to a characteristic longitudinal tear, or ribbon. This may be repeated at points along the pipeline where the explosion is relieved and then starts again the run-up to detonation.

Interpretation is complicated by the fact that a ductile failure due to a slow deflagration can create a tear which accelerates into a brittle fracture. Conversely, detonation does not necessarily cause brittle fracture.

The investigator usually seeks to determine the point of initiation of the failure. Where the failure is ductile, the point of initiation tends to correspond to that of maximum thinning. Where the failure is brittle there tend to be characteristic chevron marks on the tear which point back to the point of initiation.

With regard to source of ignition, little can be deduced from the pattern of bursting of a single vessel, but for a multi-compartment configuration the maximum damage tends to occur remote from the source of ignition.

27.7.5 Failure analysis

Failure analysis seeks to determine the details of the failure of the containment and generally involves the collection of the fragments generated by the explosion within it. An account is given by Craven, who describes the piecing together of the fragments to reconstruct the original containment and to take measurements of the thickness.

Another account of failure analysis is that of Beyers (1980), who describes the investigation of a massive explosion at a group of spherical and cylindrical storage vessels. Utilizing information on the necking of the vessels, crack propagation and fracture mechanics, it was possible to determine the order of failure of the vessels and to establish that failure had occurred because both a level measuring device and a safety

relief valve had failed, so that pumping was allowed to continue when the vessel was full and the resultant overpressure was not relieved by the safety relief valve.

27.7.6 Vapour cloud explosions

The main effect of a vapour cloud explosion which is used for diagnostics is the blast. Vapour cloud explosions tend not to give a crater and the missiles from such explosions usually yield less information than do those from confined explosions.

The characteristics of a vapour cloud explosion are described in Chapter 17. They are generally less well defined than those of a condensed phase explosion and consequently more uncertain in their application for diagnostic purposes.

A detailed survey of the damage done by the blast from the vapour cloud explosion at Flixborough has been described by Gugan (1979), who also gives an account of the interpretation of this damage to estimate the yield of the explosion. Features considered include the crushing of vessels and the bending of lampposts.

27.7.7 BLEVEs

A boiling liquid expanding vapour explosion (BLEVE) is another type of explosion which occurs in accidents in the process industries. A BLEVE tends to generate a number of fragments, but the overpressure of the blast wave is slight. There is usually relatively little difficulty in establishing that a container has undergone a BLEVE.

27.7.8 Ignition sources

It is usually more difficult to identify the source of ignition for a vapour cloud than for solid materials and in many cases of vapour cloud explosion no ignition source is identified.

27.7.9 Injury to humans

Injury to humans, whether deceased or surviving, is another potential source of information. The information which may be obtained from this source is considered by Yallop. A treatment of injury from different explosion effects is given in Chapter 17.

27.7.10 Gas explosions in buildings

An account of the investigation of gas explosions in buildings with particular reference to natural gas has been given in *Investigation and Control of Gas Explosions in Buildings and Heating Plant* (R.J. Harris, 1983). Some treatment of the topic is also given by Yallop. The account by Harris is concerned particularly with explosions following leaks of natural gas in consumers' premises.

Investigation of a gas explosion in a building proceeds by trying to establish (1) the nature of the explosion and, assuming it is a gas explosion, (2) the type of gas, (3) the source of gas, (4) the quantity, concentration and distribution of the gas, (5) the ignition source, and, frequently, (6) the pressure generated and the distribution of pressure damage.

The investigation may start by determining whether the damage has been caused by fire or explosion. Here a useful indicator is damage to windows which may have been caused by pressure or by heat. The pattern of failure of a glass window under pressure is quite different from that of failure due to heat. Pressure failure gives a large number of fragments with visible stress marks, whilst failure by heat gives fewer fragments and no stress marks. Pressure failure causes fragments to travel further and they could be found at distances of over 5m from the window.

An explosion due to gas may be distinguished from that of a bomb by the fact that the former gives a slow pressure rise and causes damage which is omnidirectional, whereas the latter gives a fast pressure and damage is greatest at the location of the bomb.

With regard to the type of gas, the principal clue is whether the gas is lighter or heavier than air, which may often be determined from a 'tide mark' of scorching.

The search for the source of gas depends on the building and the potential gas sources in it.

The quantity of gas may be estimated from the damage done both within the building and outside. Again, the behaviour of the windows provides important information. The pressure inside the building may be estimated from that required to break the windows and from the distance travelled by the fragments. The correlations used are those of M.R. Marshall, Harris and Moppett (1977) given in Chapter 17. The other indicator is damage to windows of other buildings. Here use is made of the relation for the pressure outside a vented enclosure, which decays according to a modified inverse square law, as given in Chapter 17. The pressure on these outside windows is assumed to be the reflected pressure at normal incidence, or twice the incident pressure.

The author enumerates some of the ignition sources found in consumers' premises, but states that often the ignition source is not found.

27.8 Accident Investigation : CCPS *Guidelines*

Guidance on incident investigation is given in *Guidelines for Investigating Chemical Process Incidents* (CCPS, 1992/10) (the CCPS *Incident Investigation Guidelines*).

The *Guidelines* are concerned with process safety incident investigation (PSII). They cover (1) introduction, (2) basic incident investigation techniques, (3) investigating process safety incidents, (4) practical investigation considerations (gathering evidence), (5) multiple cause determination, (6) recommendations and follow-through, (7) formal reports and communications issues and (8) development and implementation. They contain a number of appendices, including: a review of major accidents such as Bhopal, Mexico City, Piper Alpha and Pasadena; examples of the causal tree method (CTM) and multiple-cause, systems orientated incident investigation (MCSOII) method; an example incident investigation; and examples of root cause analysis.

27.8.1 Types of investigation

The CCPS *Guidelines* distinguish between three types of investigation:

Type 1 Traditional, informal investigation carried on by immediate supervisor.

Type 2 Committee-based investigation using expert judgement to find a credible solution of cause and remedy.

Type 3 Multiple-cause, systems-oriented investigation that focuses on root cause determination,

integrated with an overall process safety management (PSM) programme.

The Type 3 investigation is the preferred method.

27.8.2 Investigation management system

The *Guidelines* advocate that the company should have in place a management system for PSII. They describe the elements of this system, including the systems for incident reporting, incident classification, activating an investigation, selecting and training the investigation team, documenting the inquiry, disseminating its findings and following through its recommendations.

It is desirable that the approach to PSII be one which chimes with the methods of process safety review already in use for plant design and operation. This is met by the multiple cause analysis, or Type 3, approach, utilizing logic tree and related techniques.

The *Guidelines* give a detailed account of the measures necessary to set up a PSII management system, including the training requirements.

27.8.3 Investigation techniques

The *Guidelines* review some 18 investigation techniques which include: (1) fault tree analysis (FTA); (2) the Causal Tree Method (CTM) taken up by Rhone-Poulenc (Leplat, 1978a; Boissieras, 1983); (3) the Management Oversight and Risk Tree (MORT) method of W.G. Johnson (1980); (4) the Multiple-Cause, Systems-Oriented Incident Investigation (MCSOII) developed by Rohm and Haas (Dowell, 1990; S.E. Anderson and Skloss, 1991); (5) the Accident Anatomy Method (AAM) developed at the Riso National Laboratory (Bruun, Taylor and Rasmussen, 1979); (6) Action Error analysis (AEA) described by J.R. Taylor (1979); (7) the Cause–Effect Logic Diagram (CELD), developed by the Electrical Power Research Institute (EPRI) (Mosleh *et al*., 1988) among others; (8) hazard and operability (hazop) analysis; (9) the Accident Evolution and Barrier (AEB) technique in development at the Swedish Nuclear Power Inspectorate (Svenson, 1991a); (10) Work Safety Analysis (WSA) developed at the Technical Research Centre in Finland (VTT) (Suokas, 1981; Soukas and Rouhiainen, 1984); (11) Human Reliability Analysis (HRA) developed at Sandia National Laboratories (B.J. Bell and Swain, 1983; Swain and Guttman, 1983); (12) Multi-linear Events Sequencing (MES) developed by the National Transportation Safety Board (NTSB) (Benner, 1975); (13) the Sequentially Timed Events Plotting (STEP) procedure described by Hendrick and Benner (1987); and the Systematic Cause Analysis Technique (SCAT) developed by the International Loss Control Institute (ILCI) (1990).

Of these methods hazop, FTA, MORT, and AEA have been described in Chapters 2, 8 and 9, HRA in Chapter 14 and STEP in Section 27.4. CTM essentially utilizes a stripped-down fault tree which is applicable to the particular accident and contains only AND gates. MCSOII is also a fault tree adaptation in which the events at the level just below the top event are the presence of the injurious factor, the presence of the target and a contact duration sufficient to cause harm. AAM utilizes a tree which, like that in MORT, is generic, but which resembles a cause–consequence diagram and which is then developed to represent the features of the particular accident. AEB describes the incident in terms of a series of events in two parallel systems, the human and the technical, and of barrier functions which should prevent escalation. WSA utilizes a proforma in which are analysed the work step, hazard, causative factors, priority ranking and corrective actions. MES charts the events in a time sequence and is a forerunner of STEP. SCAT treats the incident as a domino effect and involves describing successively the loss, the contact between the injurious factor and the target, the immediate causes, the basic causes and the failure of control.

The *Guidelines* also describe other aids such as the fact–hypothesis matrix and simulation/recreation.

27.8.4 Multiple root cause analysis

Two strong themes in the *Guidelines* are that accidents have multiple causes and that the investigation should delve down to the root causes. The preferred approach is termed 'multiple cause analysis', but might equally well be called 'multiple root cause analysis'. The account given of the conduct of such an analysis relies heavily on the use of logic trees.

The *Guidelines* illustrate the application of this approach to major accidents such as Flixborough, Challenger and Piper Alpha, as well other incidents involving fire/explosion, compressor failure and vehicle collision.

27.8.5 Recommendations, reports and follow-up

The *Guidelines* discuss the recommendations of the investigation, dealing with the distinction between findings and recommendations, the correspondence between root causes and recommendations, the attributes of good recommendations, the layers of recommendations, the types of recommendation, the process of feedback on draft recommendations, the documentation of the recommendations, the recommendations on restart of plant, the documentation of the recommendations and the follow-through of the recommendations. They also treat the reporting of the incident from the initial verbal report through the interim report to the final report. The approach taken to these topics is broadly in line with that described in Section 27.5.

27.9 Public Accident Inquiries

In the UK, certain accidents are investigated by official bodies. The system varies with the industry, but in the case of a major disaster there is likely to be some form of public inquiry.

Reports of such accident inquiries include *The Flixborough Disaster* (R.J. Parker, 1975), *The Windscale Inquiry* (R.J. Parker, 1978), *MV Herald of Free Enterprise. Report of Court* (Sheen, 1987), *Investigation into the King's Cross Underground Fire* (Fennell, 1988), *Investigation into the Clapham Railway Accident* (Hidden, 1989) and *The Public Inquiry into the Piper Alpha Disaster* (Cullen, 1990). The two major disasters in the process industries which in recent years have been the subject of a public inquiry are thus Flixborough in 1974 and Piper Alpha in 1988.

In the process industries, a proportion of accidents are investigated by the HSE. Until the mid-1970s the reports of these investigations were not generally published as such, although reference was often made to them in the annual report of Chief Inspector of Factories. Following

the Flixborough inquiry in 1974, the HSE have conducted a number of major accident investigations and have published their reports, as described in Section 27.5. Thus the number of public inquiries is very small and even quite major accidents are now mainly dealt with by an HSE investigation and report.

27.9.1 Procedure at public accident inquiries

A public accident inquiry is appointed by the government minister responsible and is presided over by a judge. There is some variability in the precise form taken, but the broad pattern is that the evidence is brought forward by the counsel to the Crown who is assisted by consultants to the inquiry. The judge himself is assisted by two or three technical assessors. The terms of reference are usually to establish the cause and to make recommendations for the prevention of any recurrence.

The judge receives requests from parties who wish to be represented and then gives a ruling on who the parties are to be. Typical parties might be the operator, other industrial companies, government bodies, trades unions and representatives of survivors and relatives. Each party is represented by a barrister, typically a Queen's Counsel (QC), who is supported by a solicitor and usually by experts.

Witnesses are brought forward by Crown counsel and by other parties and can be cross-examined by the parties. In this sense the procedure resembles the adversarial process in the law courts.

27.9.2 Critique of public accident inquiries

The Flixborough inquiry (R.J. Parker, 1975) found that the disaster was due to a large release of hot, flashing cyclohexane from a 20 in. pipe, which gave rise to a massive vapour cloud explosion. This pipe was an inadequately supported bypass assembly consisting of a dog-leg pipe between two expansion bellows. The inquiry also found that this release was caused by pressure and temperature conditions in the pipe itself more severe than those which had previously prevailed. An alternative theory was put to the inquiry by Gugan and Cox that the assembly failed following prior rupture of a nearby 8 in. line, but the inquiry rejected it. A third theory was advanced at the time by R. King (1975a) that the cause was superheating of water in the reactor upstream of the pipe, but the inquiry did not pursue this hypothesis. The inquiry left proponents of these last two hypotheses dissatisfied with the way in which the technical evidence had been handled, and this gave rise to some debate in the engineering press at the time.

In consequence a view emerged and gained some support in the engineering profession that a public inquiry, with its adversarial legal process, is not the best forum in which to arrive at the truth about engineering matters. This view was urged after the Flixborough inquiry by Mecklenburgh (1977) and has been argued again with reference to the same inquiry by R. King (1990).

The critique given by King is broadly as follows. Many of the legal representatives at the inquiry are retained by interested parties. The presumption must be that the latter are concerned to protect their interests. A party may have an interest in ruling out a given cause and/or establishing another one. This situation is liable to lead to the investigation of improbable theories urged by particular parties at the expense of more probable explanations and thus to an imbalance in the investigation. Some persons whose impartial expertise would be valuable may not be called to give evidence because they are prevented by their employers or counsel or by the inquiry procedures. The inquiry itself is not accountable and there is no means of reopening it if its conclusions are subsequently found to be incomplete or incorrect.

The alternative model for technical investigation urged by Mecklenburgh draws on the procedure used in civil aviation. Aircraft accidents are investigated by the Accident Investigation Branch (AIB) of the Department of Trade. The AIB is directly responsible to the minister and is not part of the Civil Aviation Authority. The Chief Inspector of Accidents presents a report directly to the minister. The investigations of the AIB are inquisitorial not adversarial. The inspectors have considerable powers to obtain evidence and inspect wreckage. Provision is made for persons whose reputation may be affected, such as the pilot, to make representations before the report is submitted.

The Flixborough inquiry handled the investigation of certain technical aspects by using a management committee which organized meetings of technical experts. This work went on in parallel with the main inquiry. Mecklenburgh argues that it would have been both practical and preferable for the technical investigation to have been completed before the public inquiry proper. This technical investigation would have dealt with the theories concerning the cause of the rupture of the 20in. pipe. Mecklenburgh recognizes that there are usually human and management reasons for an accident. These he considers proper subjects for a public inquiry. He does not suggest that the latter be dispensed with but only that it should start only after the technical investigation has been completed. He therefore proposes that it should be required by regulation that the public inquiry be preceded by a technical investigation conducted by a specialist unit within the HSE. The technical inquiry could, of course, be dispensed with if the technical reasons for the accident are clear. This would leave the inquiry free to concentrate on the human and management aspects.

On the other hand, several engineers who have been involved as technical assessors on public inquiries have spoken in their favour. Davidson (1984), who was an assessor on the Flixborough inquiry, states:

> I do not share the view, expressed widely, that an engineer or a scientist, or a committee of them, would form a more effective Court of Inquiry than the existing type. As part of the Flixborough Inquiry there was a management committee to oversee tests and discuss the scientific side of the Inquiry. Representatives of the major parties were included. This committee was useful but very difficult to manage: everyone had preconceived ideas as to tests and how they should be run. There was not the well-established framework of rules evolved by lawyers over the centuries for orderly cross-examination. Of course some accident inquiries – e.g. for railways, mines and aircraft – are run by engineers or scientists. But such investigations have quasi-legal powers: the chairmen have by long experience become engineer/judges and conduct their inquiries much like a court of law. On balance I

was impressed by the procedure at the Flixborough Inquiry and felt that an inquiry is best run by lawyers.

Support for the present system is also expressed by Crossland (1991), an assessor on the King's Cross inquiry.

27.9.3 Piper Alpha Inquiry

The nature of a public inquiry into a major disaster may be illustrated by considering the Piper Alpha inquiry (Cullen, 1990). This was a large inquiry, as shown by some of the statistics. The inquiry sat for 180 days extending over 13 months. It heard evidence from 260 witnesses and had some 842 documents before it.

Piper Alpha involved a release of flammable gas, which ignited and exploded, and initiated a long and complex chain of escalation. The resultant emergency had many facets, including the assembly in the accommodation module and the escape and rescue. It was therefore a very different type of accident from Flixborough.

The assessors to the inquiry were an experienced oil man who had just retired as managing director of a large oil company, the production director of a large petrochemical company, and an academic specializing in safety and loss prevention but with 13 years industrial experience. The team was thus well balanced, containing two industrialists and one academic or, viewed from another angle, one from the oil industry and two from outside it.

The inquiry was in two parts. Part 1 dealt with the accident itself, its causes, its escalation and the emergency to which it gave rise, whilst Part 2 dealt with the deeper causes. Prior to Part 1 the judge announced that the inquiry would be considering in Part 2 the following subjects with a view to making recommendations: (1) the location and protection of accommodation, (2) the means of mitigating the effects of explosions, (3) the means of ensuring the integrity of emergency systems, and (4) the means of ensuring full and safe evacuation. As the evidence in Part 1 unfolded he added (5) permits-to-work, (6) control of the process, (7) risk assessment and (8) the offshore safety regime.

The assembly of the evidence was a major logistical exercise. The inquiry was seeking to determine the cause of an explosion which could have come from a leak through a hole of no more than a few square millimetres. But with most of the platform at the bottom of the sea, it was necessary to decide whether to recover the process equipment; the inquiry decided against doing this. The main accommodation module had, however, been lifted from the seabed. A major, and almost archaeological, exercise, took place to recover the documents in this module. The documents believed to be relevant to the inquiry were specified and assembled by the consultants to the inquiry who created a library available to the parties.

The interviewing of the witnesses and the preparation of witness statements was another major activity. Evidence was given to the inquiry by 58 of the 61 survivors, and the other three gave written statements. The inquiry also heard from 38 witnesses to the emergency, 5 eye-witnesses who observed and photographed events, 8 persons from other nearby installations, 32 current and former employees of the operating company on a variety of technical and management matters, 14 current and former employees of other companies, 35 expert witnesses and 6 witnesses on behalf of regulatory and other bodies.

The evidence given in Part 1 by the witnesses not called as experts covered a range of topics: the practices of the company; the activities on the platform in the preceding days; the activities and events immediately prior to the explosion; the explosion itself and its effects; the escalation of the events from the initial explosion to the abandonment of the platform; the behaviour of the communications systems and of the emergency systems for shut-down and fire fighting; the development of and response to the emergency on the platform; the escape from the platform; the response of the fire fighting vessel *Tharos* which was near the platform at that time; the response of personnel on the nearby, linked platforms; and the rescue. In many cases a single witness had significant evidence on a number of these topics.

The interim report by the Department of Energy indicated two principal hypotheses for the leak of hydrocarbons. One was that a leak occurred from the end of a relief line on a condensate pump where a pressure relief valve had been removed, because the blind flange at that point was not leak-tight or was missing altogether. The other was that liquid condensate had backed up into a reciprocating compressor and caused damage and a leak.

The inquiry began to hear expert evidence at a quite early stage, interleaved with evidence from the expert witnesses. This covered, among other things, the interpretation of eye-witness evidence on the site, fuel, nature and strength of the initial explosion; the damage to and behaviour of the emergency power and shut-down systems; the gas cloud which formed in the module; the pressures generated by and general behaviour of this gas cloud; the damage to the walls of the module; the missile effects from the explosion; the pressures and flows in the gas and oil pipelines into and out of the Piper platform; the behaviour of hydrates, with special reference to the conditions on the platform; and various aspects concerning the relief line on the condensate pumps.

As an illustration of the mix of witnesses, the first eight called were: (1) a diver (survivor), (2) a detective inspector, (3) a former deputy offshore installation manager, (4) a manager at Lloyds Register, (5) a lead maintenance technician, (6) an expert on explosion modelling, (7) an expert on gas detectors, and (8) an electrician (survivor).

In public inquiries generally the chairman is able to exercise control and ensure balance by indicating those topics in which the inquiry is interested and those in which it is not. A degree of latitude may be allowed to parties to explore particular issues. In making these decisions the chairman is advised by the assessors. At the end of the day, the final report is that of the judge alone. Nevertheless, it is the assessors' responsibility to advise him on the technical issues. In this sense an assessor has ownership of the problem. This concentrates the mind and is a strong incentive to try to make sure that evidence is as balanced and complete as possible and that the arguments are in place to support both the positive and negative conclusions. It can occur that different hypotheses for the cause are entertained until a quite late stage or that some hypotheses are discarded but fresh ones are taken on board.

Firm control was exercised in the Piper Alpha inquiry. The inquiry does not appear to have been seriously criticized either for omitting matters which ought to have been considered or for examining particular matters, and especially matters raised by interested parties, to the point of imbalance. The report shows that there was an examination of a wide range of hypothetical leak scenarios, many prompted by non-expert witness evidence, and that several fresh scenarios were given consideration, notably one in which the leak was the result of a chain of events initiated by hydrate blockage and another in which pipework suffered overpressure from a methanol injection pump. But there is little evidence of the pursuit of issues arising from special pleading by parties.

The inquiry did make use of the system of meetings of technical experts, but only on two occasions. Each was chaired by an assessor. The topics at the two meetings were flows in certain pipelines and the scenario of condensate entry into a reciprocating compressor. The purpose of the meetings was to define the areas of agreement and disagreement. In both cases there were technical reports to consider but the meeting did not deal with experimental work. At the second of these meetings the experts reached agreement that the scenario involving ingestion of liquid condensate into a reciprocating compressor could be ruled out. This conclusion was given in evidence to the inquiry and its report accepts this view.

A considerable amount of experimental work was presented in evidence. The inquiry heard about work commissioned by the operating company on the nature and strength of the initial explosion, which included explosion simulation, on the explosion damage to the fire walls, on missiles from these walls, on the failure of the Tartan gas riser and on the leak potential of various configurations of blind flange and on further explosion simulation work done for the Department of Energy. The inquiry itself commissioned wind tunnel tests to determine the gas cloud which might be expected to form given various leak scenarios and the consistency of this with the gas detector evidence. It also commissioned a single explosion simulation for a scenario of a leak at the pressure relief valve site, due either to a non-leak tight blind flange or to a hydrate-initiated event.

The *Piper Alpha Report* concluded that, on balance of probability, the leak occurred from the site of the missing pressure relief valve where the blind flange was not leak-tight. An explanation of this scenario was given which showed that it was possible to tie up quantitatively the leak rate from a non-leak-tight blind flange, the gas detector and wind tunnel evidence of a main leak preceded by a small leak, the size of the flammable gas cloud, the overpressure generated by explosion of that cloud, the damage done by the explosion, and the effects experienced in the control room from that explosion.

Among the recommendations made in the report were a change in the regulatory authority and a requirement for submission of a safety case, with a safety management system and quantitative risk assessment.

27.9.4 Role of public accident inquiries

The account given above makes clear that most accidents are in fact investigated outside the forum of a public inquiry. The HSE investigations appear in large part to accord with the intention of the system proposed by Mecklenburgh. The residual issue, therefore, concerns those process industry disasters which are on a scale sufficient to attract a public inquiry. Such disasters are rare events. They are likely to differ greatly one from another and the public inquiries held into them may, and probably should, differ also.

The experience of the Piper Alpha inquiry is instructive. The most striking thing is that the technical issues and the human and managerial issues were interwoven in several ways. In many cases a witness had evidence to give on both aspects. Witness evidence led to the consideration of fresh leak scenarios. A given scenario often involved both technical and human and managerial aspects.

Timing is another important feature. Time is required to decide on, schedule and obtain the evidence, both in documents and from witnesses, and to allow the experts to prepare their evidence, which often constitutes a mini-research project and may involve physical or computer simulation. The chairman and the assessors need time to digest the evidence and come to a settled view. The interweaving of the technical with the other evidence provides this time.

A third feature is the authority of a public inquiry. The inquiry can require the company involved to furnish documentation which may bear on the accident. The documents may be large in number, some may be hard to locate and some may be sensitive. It can require the attendance of witnesses. Once at the inquiry these witnesses are on oath. Most have probably never been in a court of law, let alone a major accident inquiry.

This authority also allows the inquiry to exercise control to try to ensure that the treatment is as balanced and complete as possible. This control is needed in respect both of interested parties and of technical experts.

Another aspect of authority relates to the fate of its report. Acceptance of the findings of the cause and of the recommendations to prevent recurrence depends in large part on the perception of the inquiry by government, the industry and the public. A public inquiry is better positioned to establish its authority than a technical investigation. This is doubly necessary where an inquiry recommends major changes in the regulatory regime or in the industry.

These considerations suggest that proposals for some form of separate technical investigation are unlikely to improve on the current form of public inquiry. What may be beneficial, however, is to recognize that there is considerable variability in the accidents which occur and that the public inquiry procedure needs to be flexible enough in its way of working to accommodate this variability.

27.10 Organizational Memory

Experience shows that the investigation of accidents is not in itself sufficient to ensure that the lessons are both learned and retained in the collective memory. It is necessary to take specific measures to ensure that this occurs. The problem is considered here from the viewpoint of a company. The arrangements necessary at national level are described elsewhere in this chapter.

Table 27.3 *Some recurring themes in accident investigation (after Kletz)*

A Some recurring accidents associated with or involving
Identification of equipment for maintenance
Isolation of equipment for maintenance
Permit-to-work systems
Sucking in of storage tanks
Boilover, foamover
Water hammer
Choked vents
Trip failure to operate, neglect of proof testing
Overfilling of road and rail tankers
Road and rail tankers moving off with hose still connected
Injury during hose disconnection
Injury during opening up of equipment still under pressure
Gas build-up and explosion in buildings
B Some basic approaches to prevention
Elimination of hazard
Inherently safer design
Limitation of inventory
Limitation of exposure
Simple plants
User-friendly plants
Hazard studies, especially hazop
Safety audits
C Some management defects
Amateurism
Insularity
Failure to get out on the plant
Failure to train personnel
Failure to correct poor working practices

Approaches to the problem are discussed in *Lessons from Disaster* by Kletz (1993b) and (1980g, 1982j, 1993c), R.W. Fawcett and Kletz (1982) and Hancock (1989, 1992).

The reduction of accidents is to a large extent a matter of applying what is already known. Unfortunately within an organization this knowledge often decays. Sometimes it is an individual who is unaware, even though the matter is well known in many parts of the organization. Sometimes the organization as a whole appears to have forgotten. In Kletz' words 'Organizations have no memory'.

Kletz has also put the matter even more graphically. During his time as a safety adviser he was often tempted to tell a manager on whose plant a familiar accident had happened: 'Don't bother to write the accident report. I'll send you a copy from my files.'

The first step in countering this problem is to ensure that the right lessons are drawn about the accidents which have already occurred, in the company and elsewhere. The need to get down to the fundamental causes was the main theme of Sections 27.5 and 27.8.

Measures aimed at making sure that the lessons are not forgotten but remain fresh in the collective memory are described by Kletz (1993b). Starting from receipt of the report, they may be summarized as follows. The immediate actions should be to (1) follow up the recommendations, and (2) publicize the lessons. In order to keep the accident fresh in the memory steps should be taken periodically to (3) hold workshops in which it is discussed, and (4) describe it in the company safety and loss prevention newsletter. Measures may also be taken to (5) introduce a reference to the accident in any code which contains provision derived from it, and (6) create a database of accident case histories which gives company personnel easy access to them. Management should (7) avoid turning a blind eye to unacceptable work practices, and (8) before removing equipment or ending a procedure find out what its original purpose was.

There are a number of recurring themes in accident investigation and it is helpful to be aware of these. Some themes which run through the work of Kletz and which he has highlighted explicitly are shown in Table 27.3.

27.11 Case Histories

Case histories are critical to the learning process. Without this lifeblood the process would soon shrivel and die. Case histories, and their sources, are described in Appendix 1.

27.12 Information Exchange

Learning can take place only if information on accidents and accident investigations is made freely available by the publication of reports and by schemes for information exchange.

27.12.1 *Loss Prevention Bulletin*

A principal information exchange scheme is that operated by the Loss Prevention Panel of the Institute of Chemical Engineers (IChemE). The *Loss Prevention Bulletin* (LPB) published by the panel contains articles on various aspects of safety and loss prevention, but above all it gives case histories of accidents with accompanying analyses. The titles of the articles in the bulletin are listed after the references given at the end of this book.

27.12.2 Trend in publication

According to Kletz (1993b), the number of accident case histories published is diminishing. Unless this trend is reversed, the industry's learning process will be severely impaired.

Kletz deals in detail with the justification for the publication of accident reports, the reasons for the fall-off and the measures which should be taken to counter it.

27.13 Accident Databases

The accessibility of accident case histories is much enhanced by the creation of accident databases, particularly computer-based databases.

27.13.1 Major databases

There are a number of major accident databases such as the Major Hazard Incidents Data Service (MHIDAS), the Explosion Incidents Data Service (EIDAS) and the Environmental Incidents Data Service (EnvIDAS) of the Safety and Reliability Directorate (SRD); the Failure and Accident Technical Information System (FACTS) of TNO; the Major Accident Reporting System (MARS) of the Commission of the European Communities (CEC); and World Offshore Accident Database (WOAD) of Veritas Offshore Technology. An account is given in Appendix 1.

27.13.2 Company databases

A number of companies have developed their own accident databases, either confined to accidents which have occurred in the company or extended to include other accidents. An account of such a database in ICI has been given by R.W. Fawcett and Kletz (1982).

27.14 Safety Performance Measurement

Turning from accident investigation to the feedback of information about safety performance in a company, the first requirement is for methods of measuring it. Accounts of safety measurement are given in *Managing Safety* (HSE, 1981d) and *Techniques of Safety Management* (D. Petersen, 1989).

27.14.1 Safety performance metrics

The safety performance criteria which it is appropriate to use are discussed in Chapter 6. For personal injury, the injury rate provides one metric, but it has little direct connection with the measures required to keep under control a major hazard. For the latter what matters is strict adherence to systems and procedures for such control, deficiencies in the observance of which may not show up in the statistics for personal injury. However, as argued in Chapter 6, there is a connection. This is that the discipline which keeps personal injuries at a low level is the same as that required to ensure compliance with measures for major hazard control.

There needs, therefore to be a mix of safety performance criteria. Those such as injury rate have their place, but they need to be complemented by an assessment of the performance in achieving safety-related objectives. Safety performance criteria are discussed in detail by Petersen. Different criteria are required for senior management, middle management, supervisors and workers. He lists the desirable qualities of metrics for each group.

Any metric used should be a valid, practical and cost-effective one. Validity means that it should measure what it purports to measure. One important condition for this is that the measurement system should ensure that the process of information acquisition is free of distortion.

Qualities required in a metric for senior management are that it is meaningful and quantitative, is statistically reliable and thus stable in the absence of problems, but responsive to problems, and is computer-compatible.

For middle management and supervisors the metric should be meaningful, capable of giving rapid and constant feedback, responsive to the level of safety activity and effort, but sensitive to problems.

A metric which measures only failure has two major defects. The first is that if the failures are infrequent, the feedback may be very slow. This is seen most clearly where the criterion used is fatalities. A company may go years without having a fatality, so that the fatality rate becomes of little use as a measure of safety performance. The second defect is that such a metric gives relatively little feedback to encourage good practice.

A safety performance metric may be based on activities or results. The activities are those directed in some way towards improving safety practices. The results are of two kinds, before-the-fact and after-the-fact. The former relates to the safety practices, the latter to the absence or occurrence of bad outcomes such as damage or injury.

Metrics for activities or before-the-fact results may be based on the frequency of some action such as an inspection or the frequency of a safety-related behaviour such as failure to wear protective clothing. Or they may be based on a score or rating obtained in some kind of audit.

27.14.2 Some incident-based metrics

There are numerous metrics which can be devised based on incidents such as damage or injury. The first requirement for such a measure is a clear definition of the events to be recorded.

The incidents measured may include various forms of injury event and reportable accidents. Types of injury event include first aid treatments, lost time accidents, serious injury accidents, and fatalities. Types of reportable accident are those for which there are statutory reporting requirements and those for which there is in addition a company reporting requirement.

Some metrics commonly used in the UK include

$$M_1 = n_{\mathrm{ra}}/N_{\mathrm{p}} \qquad [27.14.1]$$

$$M_2 = N_{\mathrm{lta}}/N_{\mathrm{h}} \qquad [27.14.2]$$

$$M_3 = n_{\mathrm{hl}}/N_{\mathrm{h}} \qquad [27.14.3]$$

where M_1, M_2 and M_3 are metrics, n_{hl} is the number of hours lost, n_{lta} is the number of lost time accidents, n_{ra} is the number of reportable accidents, N_{h} is the number of hours worked and N_{p} is the number of persons at risk.

27.14.3 Organization of measurement

There needs to be a formal system for the measurement of safety performance. This may be organized in various ways. In particular, systems differ in the division of responsibility between line management and the safety function.

It is normal for line management to measure, and report on, production performance and it may well do the same on safety performance. This is the preferred method in the arrangements described by the HSE (1981d). If it is adopted, its operation should be subject to audit by the safety function.

The HSE states 'The most frequently encountered difficulty in applying measuring schemes is for a manager to separate his own performance as an individual from that of his team'. The way in which this problem is resolved depends on the culture of the particular company.

27.15 Safety Performance Monitoring

Given that performance is to be assessed by measuring events, such as failures or accidents, then probability theory may be used to determine whether there has been an improvement or deterioration in performance as between two situations.

27.15.1 Statistical measures

An account of the methods which may be used to detect changes of performance has been given by Wynn (1950).

If over a given reference period in a population of size n the observed number of events x has been sufficiently large that the expected number of events, μ $(= x/n)$ is firmly known, then the Poisson distribution is applicable

$$P(r) = \exp(-\mu)\frac{\mu^r}{r!} \qquad [27.15.1]$$

where $P(r)$ is the probability of r events. The application of Equation [27.15.1] is facilitated by the use of Figure 27.3, which gives the observed number of events vs the expected number of events. It should be noted that although the curves drawn are continuous, the events to which they apply are integers.

As an illustration of the use of Figure 27.3, consider the case where the expected number is 8. If the observed number is 10, the difference is not significant, but if the observed number is 15, this is significant at the 95% level.

The use of the Poisson distribution in this way is permissible only if the expectation μ is known. The confidence with which the expected number of events is known depends on the observed number of events in the reference period. The determination of the confidence limits for the frequency of an event for use in the exponential or Poisson distribution was described in Chapter 7. Tables of the confidence limits of the Poisson distribution have been given by Woodcock and Eames (1970 UKAEA AHSB(S) R179).

If there is no firm expectation, the Poisson distribution is not applicable, but the problem may be treated using the chi-square distribution. This distribution may be used to test the hypothesis that there is no difference between a reference period and a test period where the population size and the number of events in the reference period are n_1 and x_1 and those in the test period are n_2 and x_2, respectively. For this case the following chi-square table is applicable:

	No. affected by event	*No. unaffected by event*	*Total*
Population 1	x_1	$n_1 - x_1$	n_1
Population 2	x_2	$n_2 - x_2$	n_2
Totals	$x_1 + x_2$	$n_1 + n_2 - x_1 - x_2$	$n_1 + n_2$

A particular formulation of chi-square for this case (Moroney, 1956, p.255) is

$$\chi^2 = \frac{[x_1(n_2 - x_2) - x_2(n_1 - x_1)]^2(n_1 + n_2)}{n_1 n_2 (x_1 + x_2)(n_1 + n_2 - x_1 - x_2)} \qquad [27.15.2]$$

$$\approx \frac{(x_1 - kx_2)^2}{k(x_1 + x_2)} \qquad n_1 \gg x_1,\ n_2 \gg x_2 \qquad [27.15.3]$$

with

$$k = n_1/n_2 \qquad [27.15.4]$$

The system described here has one degree of freedom, and for this the values of chi-square are

Confidence level	χ^2
90%	2.706
95%	3.841
99%	6.635

The application of equation [27.15.3] is facilitated by the use of Figure 27.4, which gives the group $(x_1 - kx_2)$ vs the group $k(x_1 + x_2)$.

As an illustration of the use of Figure 27.4, consider the case where in the reference period the population size is 1000 and the number of events is 55, and in the test period the corresponding values are 1000 and 45. Then the values of k and of the groups $(x_1 - kx_2)$ and $k(x_1 + x_2)$ are 1, 10 and 100, respectively. This difference is not significant, but if the numbers of events in the reference and test period are 60 and 40, respectively, the difference is significant at the 95% level.

The chi-square method becomes inaccurate if the number of events in the cells of the chi-square table falls too low. The number should exceed about 20, or for approximate work about 5.

It should be noted that the quantity investigated using the methods just described is the number of events, not the event rate. It is also emphasized that the validity of any conclusions drawn depends on the correct choice of the variable which describes the population size. If in a particular case, for example, it is assumed that the number of maintenance accidents depends on the number of maintenance personnel, whereas in reality it depends on some other factor such as the number of maintenance tasks done, then incorrect conclusions may be drawn.

27.15.2 Vigilance against rare events

The more serious accidents are rare events, and the absence of such events over a period must not lead to any lowering of guard. There needs to be continued vigilance.

The need for such vigilance, even if the safety record is good, is well illustrated by the following extract from the 'Chementator' column of *Chemical Engineering* (1965 Dec. 20, 32):*

> The world's biggest chemical company has also long been considered the most safety-conscious. Thus a recent series of unfortunate events has been triply shattering to Du Pont's splendid safety record.
>
> Latest incident occurred earlier this month when a dust explosion and flash fire in a dyestuff drying machine at the company's immense Chambers Works, Deepwater, N.J., caused some $50 000 damage, claimed two lives

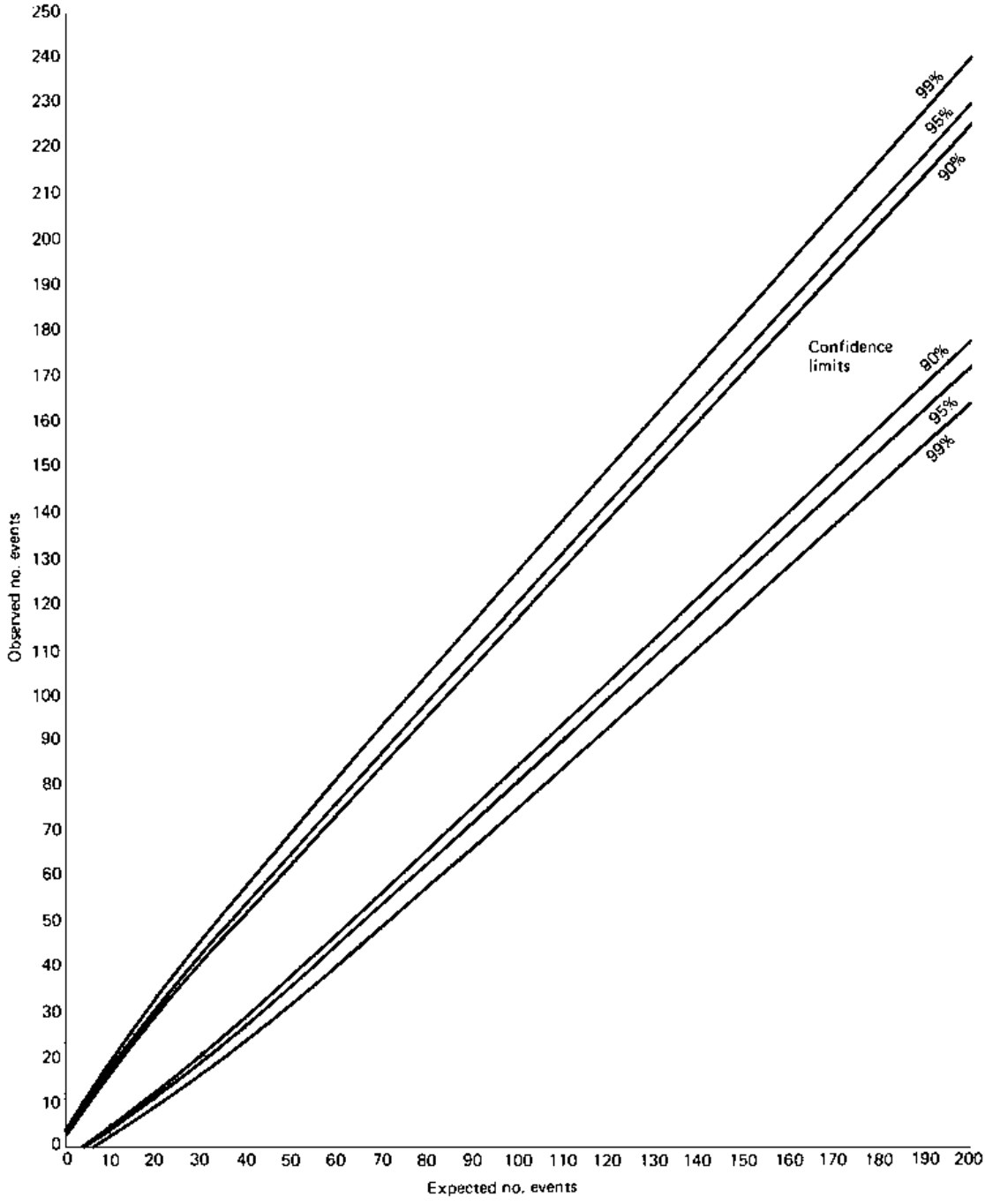

Figure 27.3(a) *Graph (coarse scale) for the determination of trends in safety performance: Poisson distribution (after Wynn, 1950)*

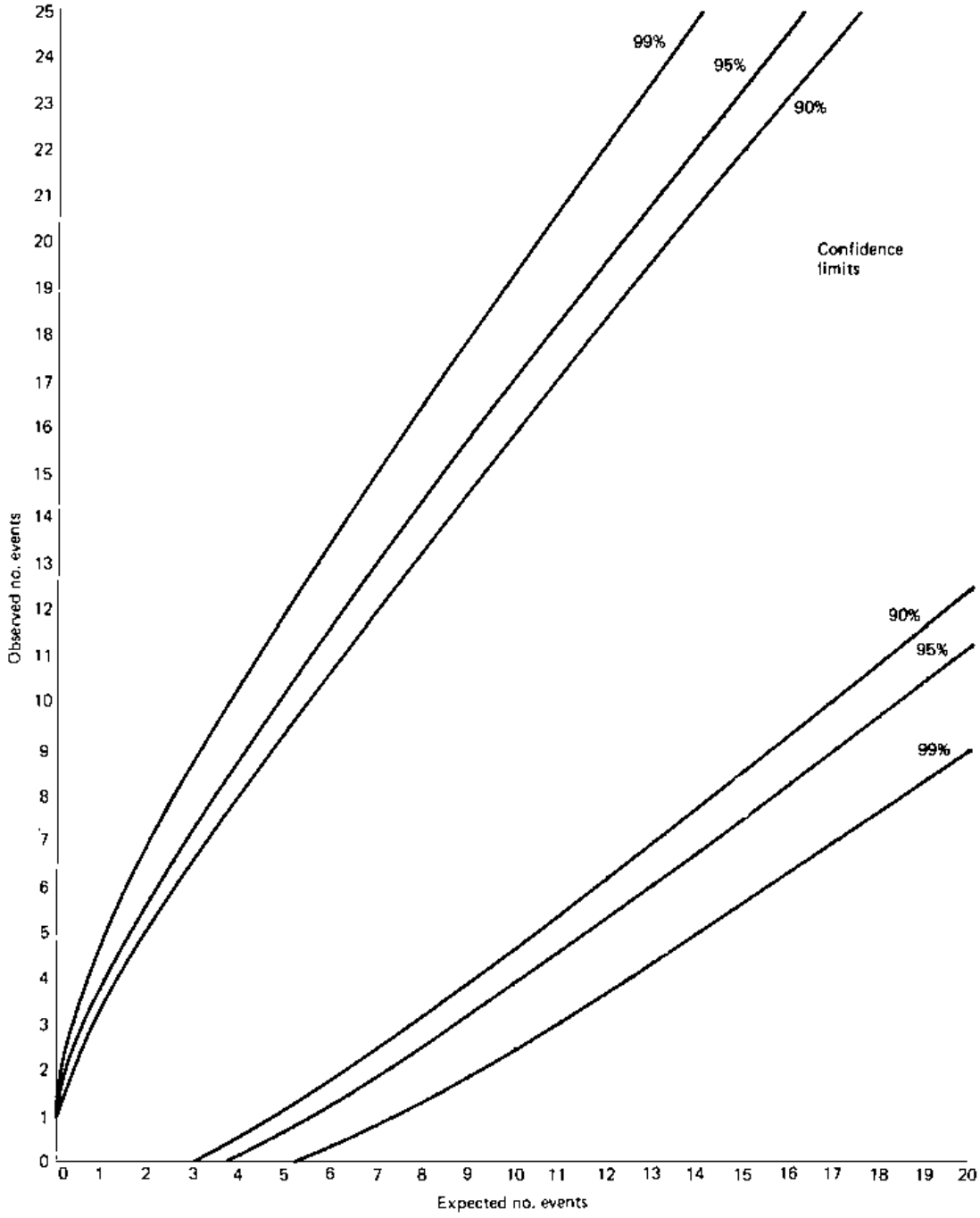

Figure 27.3(b) *Graph (fine scale) for the determination of trends in safety performance: Poisson distribution (after Wynn, 1950)*

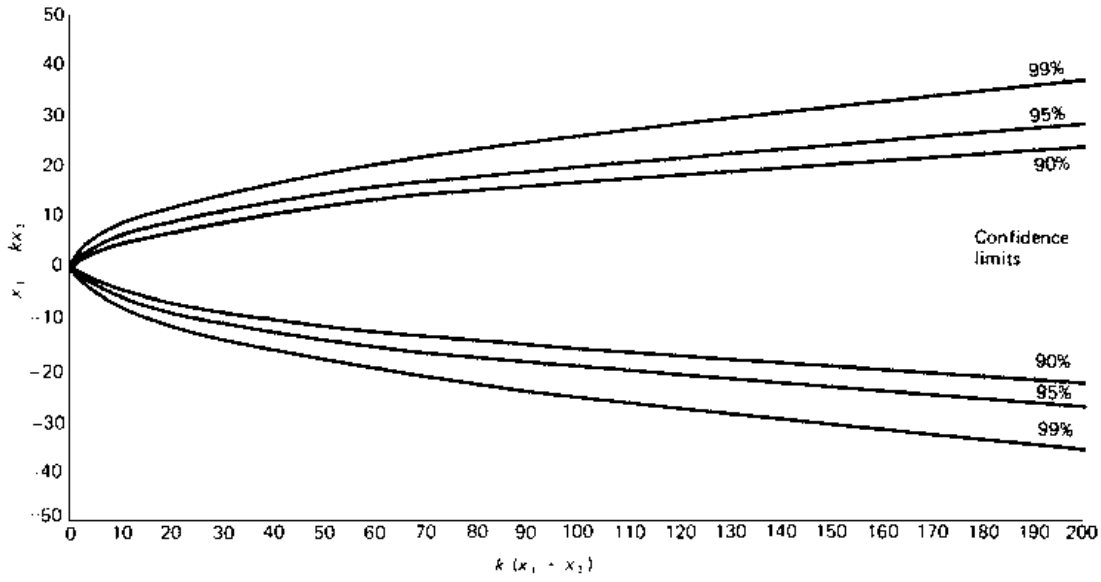

Figure 27.4 *Graph for the determination of trends in safety performance: chi-square distribution (after Wynn, 1950)*

and injured nine more, three seriously. Ironically, in August of this year the plant had received an award from the governor of New Jersey for achieving 16 771 355 man hours worked without a single lost time accident.

In late November, a flash fire swept the drying room of the company's Carney Point, N.J., gunpowder plant. Damage was relatively light but four workmen perished. In operation before the turn of the century, the plant had had no fatal accidents since before World War I.

The earliest of the triple tragedies was a blast and fire at the firm's Louisville plant in August. Claiming 11 lives and causing $5 to $10 million damage, the accident's magnitude was without precedent in the company's history.

*Reproduced with permission of *Chemical Engineering*.

27.16 Near Miss Reporting

It has long been appreciated that for every accident there are many lesser events, some with less material effect and others with no effect at all, and that is desirable to learn from these 'near misses'.

Accounts of the monitoring of and learning from near misses are given in *Near Miss Reporting as a Safety Tool* (van der Schaaf, Lucas and Hale, 1991) and by N. Carter and Menckel (1985).

Near Miss Reporting contains in effect a debate on the subject and poses the question of the purpose of such reporting.

27.16.1 Licensee Event Reports

One of the main public sources of information on near misses is the Licensee Event Reporting system of the Nuclear Regulatory Commission. Analyses of Licensee Event Reports (LERs) have been given by Rasmussen (1980b), who has also used the information given in these reports in his development of a methodology for the handling of human error.

27.16.2 Models for reporting

A system of near miss reporting must specify in some way the events to be reported and must therefore be based, explicitly or implicitly, on some form of model. Three principal forms of model are (1) the engineering system, (2) human behaviour, and (3) the managerial and organization factors. Each type of model is represented in the account which follows.

27.16.3 Aims of reporting

It is suggested by van der Schaaf (1991c) that near miss reporting may be undertaken for three different purposes: (1) modelling (qualitative insight), (2) monitoring (quantitative insight), and (3) motivation (maintaining alertness).

If the aim is modelling, the interest centres on reporting of 'new' types of near misses, whereas if it is monitoring, the implication is that it is known types which are reported. The third aim, motivation, differs from the other two in that it is essentially a by-product of the reporting, albeit an intended one. The activity of reporting near misses makes people more conscious of them.

The author gives an account of a near miss management system which is aimed at monitoring rather than modelling, but which should have as a by-product an

increase in motivation amongst those involved in the reporting.

27.16.4 Near miss management system

A description is given by van der Schaaf (1991b) of a near miss management system (NMMS). The concepts underlying this are that its sole function should be as a means for the organization to learn from near misses, that is should have as comprehensive a coverage as possible of the inputs and outputs, that it should be based on a suitable model of human behaviour, and that it should be integrated into, rather than grafted onto, the organization.

The modules of the framework for the NMMS are:

(1) Detection: recognition and reporting.
(2) Selection: according to purpose(s).
(3) Description: all relevant hardware, human and organizational factors.
(4) Classification: according to a socio-technical model.
(5) Computation: statistical analysis of large database of incidents to uncover certain (patterns of) factors.
(6) Interpretation: translation of statistics results into corrective and preventive measures.
(7) Monitoring: measuring the effectiveness of proposed measures after their implementation.

Further features of the NMMS are described by van der Schaaf (1991a) in an account of its application in a chemical plant, and specifically in the central control room. The detection module is essentially a redesigned version of an existing near miss reporting system. The selection module allocates the event to the modelling or monitoring mode. The description module utilizes a form of fault tree, termed an incident production tree, which contains as elements not only faults and errors but also recoveries, as described elsewhere by van der Schaaf (1988). The classification module is based on Rasmussen's skills-rules knowledge SRK model of human behaviour. The classification proceeds in two stages. In the first stage a rough classification is made into (1) technical factors, (2) organizational factors and (3) behavioural factors. Each element in the incident production tree is then examined according to the following procedure. It is first considered for classification as a technical factor, and if it is such it is assigned to a subcategory such as engineering, construction, etc.; if this does not apply, it is considered for classification as an organizational factor; if this also does not apply, then, and only then, is it considered for classification under the third category as a behaviour factor.

27.16.5 Computer aid for reporting

The practicalities of near miss reporting and a computer-based aid influence diagram analysis (IDA) for such reporting are described by A.R. Hale *et al.* (1991). This work complements that of van der Schaaf just described and utilizes the same framework modules.

A problem with near miss reporting is that if a proforma is used, most of the entries are not relevant to a given event. This can be overcome by the use of a computer aid in which the user is prompted to enter information interactively.

The accident model used in this case is a hybrid derived partly from the energy barrier concept found in MORT (W.G. Johnson, 1980) and partly from the concept of deviation from normal conditions (Kjellen, 1983; A.R. Hale and Glendon, 1987).

27.16.6 Critiques of reporting

A critique of near miss reporting has been given by Reason (1991), who argues that current reporting schemes, where they exist, tend to be relatively ineffective in supporting safety management.

He distinguishes between active failures which have an immediate adverse effect, and latent failures which lie as dormant, enabling conditions until the accident is triggered by an active failure. He likens latent failures to resident pathogens in the human body. He argues that the most effective approach to the prevention of accidents is to identify and neutralize these pathogens.

Reason utilizes an accident model in which a distinction is made between failure types and failure tokens. In essence, the failure types are general classes of managerial and organizational failure, whilst the tokens are specific failures of individuals. The latter are categorized as slips and lapses, mistakes and violations.

He considers five channels for system safety information. These channels are (1) accident and incident reporting systems, (2) unsafe act and near miss reporting systems, (3) precursors of unsafe acts, (4) failure type indicators and (5) stylistic or cultural indicators. The precursors of channel 3 are described in terms similar to those applied to performance shaping factors. The failure types of channel 4 are the classes of managerial failure. The cultural indicators of channel 5 are described in terms of a seven-point ranking scale, which ranges from a condition where safety practices are at the barest industry minimum to one where good practice is followed.

The general failure types are (1) hardware defects, (2) design failures, (3) poor maintenance procedures, (4) poor operating procedures, (5) error-enforcing conditions, (6) poor housekeeping, (7) incompatible goals, (8) organizational failures, (9) inadequate training, and (10) inadequate defences.

Reason argues that the key to effective safety management lies in appreciating what is controllable and what is not. He contrasts the situation in respect of accidents with that pertaining in production. Most of the factors which affect production are under the control of management. Accidents are different. They arise from a complex interaction between latent failures and local triggering events. There is little management can do about the latter. It should concentrate on the former, and any near miss reporting system should reflect this. What should be reported are failures at the level of channels 4 and 5.

The need to base near miss reporting on an appropriate model is echoed by Lucas (1991), who proposes reporting based either on the man-machine interface or on system-induced error.

27.16.7 Hazard warning structure

Another approach to near miss reporting is the hazard warning structure developed by Lees (1982b, 1983b, 1985). The basic concept is that the undesired event is modelled using a hazard warning tree, a specialized form of fault tree, so that the place of lesser events in the hazard warning structure can be seen. An account of

hazard warning structure with examples is given in Chapter 9.

The hazard warning concept is intended to be used first in the design of plant and to be then carried through into its operation. If at the design stage an analysis has been made of the hazard warning structure for the undesired events of interest, it is then possible to use the analysis to locate lesser events as they occur in the structure, to assess their significance and to take measures to control them.

The hazard warning structure approach is based on, and oriented to, fault trees for engineering systems. By comparison with the near miss reporting just described, it has the following distinguishing characteristics. The events to be monitored are decided in advance and are relatively well defined. Other events not included are not monitored, at least not as part of this particular exercise. The method does not address human errors as such but rather the effects of such errors on the engineering system.

The incident production tree described above evidently has features in common with the hazard warning tree.

27.17 Education

The education of engineers normally includes some material on safety. In chemical engineering this has traditionally tended to cover aspects such as legal requirements and personal safety. There has also generally been some coverage of the engineering aspects, particularly in design projects, but overall the treatment has been variable.

The occurrence of disasters such as Flixborough, Seveso and Bhopal has highlighted the need for greater awareness of and knowledge about safety and loss prevention (SLP). These three accidents have had particular impact in the UK, Continental Europe and the USA, respectively. The trend has been for industry to urge universities to teach SLP and for professional bodies to introduce a requirement that SLP be part of the curriculum.

Accounts of the treatment of SLP in university courses in chemical engineering have been given by Mewis (1984), Talty (1986), Kaufmann (1987), Kletz (1988l, 1990a), Crowl and Louvar (1989), Nolan (1989), V.C. Marshall (1991c), Crawley and Scott (1992) and Lemkowitz (1992a,b).

The inclusion of SLP in chemical engineering curriculum requires justification. The ACMH in its *Third Report* (Harvey, 1984) stated:

> It is important that students be introduced to the concept of inherently safer design and that they realize that safety in plant operation must be considered right at the start of the design study. Process safety must be taught in a rigorous, stimulating way by staff of appropriate experience. Departments which initially do not have this expertise may need to use the services of experts from other universities, industry and consulting firms. By virtue of the nature of processes which give rise to major hazards, it is the chemical engineer who often fills the position of responsible person in the design or operation of plant. (paragraph 124)

Support for this view is given by Kletz (198l), who advances three principal arguments. One is the importance of treating safety from the outset as an integral part of the design of plant and of aiming for inherently safer design. Another is that whatever use he may make of other subjects taught at university, any practising chemical engineer will be involved in safety matters. He has a moral and legal responsibility and will probably be faced with safety issues from the first day. The third is that SLP involves basic principles.

SLP involves the application of a quantitative approach and encourages numeracy. It is based on a structured approach which involves the identification of hazards, an estimation of their frequency, an estimation of the consequences, and decision-making based on defined criteria.

The need for an engineer to take a wider view of the task in hand is emphasized by Crawley and Scott (1992). Industry requires someone who is capable of reasoning and is aware of the factors involved and of the pitfalls. For example, in a design the student may well be able to calculate a flow in a pipe, but fail to give consideration to erosion, vibration, noise, or isolation for maintenance.

The need to achieve a cost-effective design is another factor. There is often almost no end to the safety measures which might be taken. The engineer needs a tool which assists in deciding how far to go.

The view exists that even if the need for education in SLP is accepted, it is better done when the engineer first enters industry. However, the chemical engineer may well enter a firm which lacks the means of bringing him up to the level of SLP awareness and capability achievable at university, or one which does not have a safety culture. Even larger companies generally favour its inclusion in the university course. This does not, of course, obviate the need for the company to carry out its own training in SLP, particularly for new entrants.

The extent to which SLP ranks as a mainstream subject in chemical engineering has been examined by V.C. Marshall (1991c). He argues that to qualify a subject must meet the following criteria. It should (1) be acknowledged as such by the academic culture, (2) be recognized as relevant by students, (3) be intellectually demanding, (4) comprise a well established corpus of knowledge, organized on clearly defined unifying principles, (5) be highly quantitative and thus capable of being subjected to mathematical analysis, (6) possess a content and unifying principles set out in authoritative textbooks, (7) be taught by specialists, (8) be a compulsory subject which must normally be passed, and (9) be examined formally. He goes on to consider the extent to which SLP now meets these criteria. V.C. Marshall (1987, 1989c, 1990d) has also attempted to develop the unifying structure which he calls for.

Some objectives to be attained in teaching SLP and means used to achieve them include:

Awareness, interest	Case histories
Motivation	Professionalism
	Legal responsibilities
Knowledge	Techniques
Practice	Problems
	Workshops
	Design project

There has been considerable debate as to whether SLP should be taught by means of separate course(s) or as part of other subjects. The agreed aim is that it should be seen as an integral part of design and operation. Its treatment as a separate subject appears to go counter to this. On the other hand, there are problems in dealing with it only within other subjects. It cannot be expected that staff across the whole discipline will have the necessary interest, knowledge and experience and such treatment is unlikely to get across the unifying principles. These latter arguments have weight and the tendency appears to be to have a separate course on SLP but to seek to supplement this by inclusion of material in other courses also. It is common ground that SLP should be an essential feature of any design project.

In 1983 the IChemE issued a syllabus for the teaching of SLP within the core curriculum of its model degree scheme. This syllabus was:

> *Safety and Loss Prevention*. Legislation. Management of safety. Systematic identification and quantification of hazards, including hazard and operability studies. Pressure relief and venting. Emission and dispersion. Fire, flammability characteristics. Explosion. Toxicity and toxic releases. Safety in plant operation, maintenance and modification. Personal safety.

In 1988 the IChemE issued further suggestions for the teaching of SLP. The background to these is given by Nolan (1989) and Crawley and Scott (1992), who also give an outline of the material proposed.

The topics highlighted by Kletz (1988l) as core material in SLP are inherently safer design, hazop, hazard analysis, human error, and maintenance and modification.

The emerging pattern in the introduction of SLP into undergraduate courses appears to be an elementary treatment, perhaps within an overview course on chemical engineering, early on followed at some later point by a dedicated course on SLP. This is the approach described by Crawley and Scott and by Lemkowitz (1992a,b).

Another subject which has many similarities to SLP is environmental protection. These similarities include the engineer's moral and legal responsibilities, the concept of inherently cleaner design, and a structured approach to environmental risks. There is a discernible trend, therefore, to treat environmental protection in a manner broadly similar to, and sometimes in the same course as, SLP.

The inclusion of SLP within a university chemical engineering course is not without its problems. One is the allocation of time within the timetable. The order of contact hours typically mentioned is some 4 hours for elementary treatment early on and 20 hours for a later dedicated course.

The other main problem is the availability of staff able and willing to teach SLP. Such teaching requires both industrial experience and knowledge not only of the specific discipline of SLP but of a number of core subjects. Only a small proportion of departments contain staff specializing in the subject. It is recognized, therefore, that there is need for support for staff teaching SLP. Two principal forms of support are the use of engineers from industry to complement the academic teaching and the provision of teaching material on the subject.

Table 27.4 *Some links between safety and loss prevention and other subjects in chemical engineering*

SLP topic	Regular subject
Inherently safer design:	
Chemical reactors	Reaction engineering
Separation processes	Mass transfer
System failure	Reliability engineering
Failure rates	Probability theory
Pressure vessels	Properties of materials: Strength of materials Fracture mechanics
Chemical reactors:	
Reaction runaway	Reaction engineering
Instruments	Instrumentation
Venting	Fluid mechanics: two-phase flow
Trip systems:	Instrumentation
Trip failure	Reliability engineering
Trip response	Process dynamics
Process operator	Human factors
Emission:	
Relief valve discharge	Fluid mechanics: gas flow
Flashing liquid	Fluid mechanics: two-phase flow
Vessel burst	Mixing processes
Vaporization:	
Volatile liquid	Simultaneous heat and mass transfer
Cryogenic liquid	Unsteady-state heat transfer
Dispersion	Turbulence theory
Fire	Radiant heat transfer
Explosion:	
Explosion energy	Thermodynamics
Adiabatic flame temperature	Thermodynamics
Toxicity:	
Toxicity testing	Probability theory
Computer aids:	
Plant design	Expert systems
Fault tree synthesis	Graph theory
Valve sequencing	AI techniques
Pressure systems management	Management
Risk criteria	Engineer in society

SLP can serve as an integrating factor in a course. In this respect it has much in common with a design project. Some of the regular chemical engineering subjects on which the teaching of SLP draws are

(1) mathematics;
(2) thermodynamics;
(3) fluid mechanics;
(4) mass transfer;
(5) heat transfer;
(6) reaction engineering;
(7) particle science and technology;
(8) process instrumentation;
(9) process dynamics and control;

Table 27.5 *Some training aids for safety and loss prevention available from the IChemE*

001	Hazards of Over- and Under-Pressuring of Vessels (SL)
002	Hazards of Plant Modifications (SL)
003	Fires and Explosions (SL)
004	Preparation for Maintenance (SL)
005	Furnace Fires and Explosions (SL)
006	Preventing Emergencies in the Process Industries (V, SL)
007	Work Permit Systems (SL, B)
008	Human Error (SL, B)
009	Inherent Safety (V, SL, B)
010	Handling Emergencies (CS)
011	Safe Handling of LPG - Pt 1: Pressurized Bulk Storage and Road and Rail Loading (V, SL)
012	Safer Piping - Awareness Training for the Process Industries (V, SL)
013	Safe Handling of LPG - Part 2: Ship/Shore Transfer and Refrigerated Storage (V, SL)
014	Practical Risk Assessment (OL)
015	Hazop and Hazan (SL, B)
016	Controlling Electrostatic Hazards (V, SL)
017	Managing for Safety (V, SL)
018	Safer Use of Chemical Additives (SL)
019	Offshore Practical Risk Assessment (OL)
020	Learning from Accidents (SL)
021	Flammable Liquid Fire . . . Don't be a Victim (V)
022	Dust Explosion Hazard (V, SL, B)
023	Control of Exothermic Chemical Reactions (V, SL, B)
024	Tank Fires (SL)
E04	Environmental Auditing (SL)

[a] B, Book; CS, computer simulation module; OL, open learning module; SL, slide training module; V, video training module.

(10) human factors;
(11) computer methods;
(12) management;
(13) engineer in society.

Table 27.4 illustrates some of the links between SLP topics and regular chemical engineering subjects.

Accounts of practice in particular courses are given by Kaufmann (1987), Kletz (1988l) and Lemkowitz (1992a,b). Kaufmann describes the use of a number of mini-courses, taking some 10–15 minutes. The treatment described by Lemkowitz involves an integrated treatment of SLP and environmental protection and has three main parts. In the first, early part a problem is taken from the media or the literature and becomes a project for investigation by the student which involves interviewing industrial personnel about it. The second part is a dedicated course of lectures taking some 24 hours. The third part is a safety report which is submitted prior to starting on a laboratory project.

27.18 Teaching Aids

There are available a number of teaching aids of various kinds, suitable for use in the education of engineers at universities and/or of engineers and other personnel in industry.

Short introductions to safety and loss prevention are given in *Flowsheeting for Safety* (Wells, Seagrave and

Table 27.6 *Some training aids for safety and loss prevention: films and videos*

A HSE
It Shall be the Duty (HSWA 1974)
All in a Day's Work (work of Factory Inspectorate)
Health at Work (work of EMAS)
Protection of Eyes Regulations
Guarding Machinery
Principles of Machinery Guarding
A Guide to Interlocking Guards
Abrasive Wheels
Watch that Space: Confined Space Hazards in Factories
Control of Exothermic Chemical Reactions
B Fire Protection Association
Understanding Fire
C Amoco
Hazard of Air
Hazard of Water
D British Gas
The Science of Flame – Principles
The Science of Flame – Control
The Frigg Story
Too Good to Waste (North Sea gas)
The Innovators
E Conoco UK Ltd
The Murchison Project (offshore oil)
F Millbank Films (ICI)
If One Green Bottle (management responsibility)
Something to do with Safety Reps
Talking of Safety (safety committees)
When Fire Starts
Toxic Hazards in Industry
Permit-to-Work
Is There Anything I've Forgotten? (permit-to-work systems)
Incident Rendered Safe (transport emergencies)
Better than Cure (occupational health)
Safeguard (machine guarding)
One Last Shock (electrical safety)
Make Light of Lifting
Mind Your Back (lifting)
It Need not Happen (protective clothing)
Air to Breathe (breathing apparatus)
Rescue Team Alert
One Million Hours (accident investigation)
Nobody's Fault (story of an accident)
Flashpoint (laboratory safety)
G Shell
Oil Refinery
Principles of Refining
Petrochemicals: the Building Blocks
Petrochemicals: Polymerization Reactions
H Total Oil Great Britain Ltd
Petroleum, its Refining

Flames of the Desert (Middle East oil)
Before the Derricks Rise (offshore oil)
The Riddle of the Deep (offshore underwater)
I UK Atomic Energy Authority
Principles of Fission
The Nuclear Fuel Cycle
Safety and Nuclear Power
Nuclear Fuel Reprocessing

Whiteway, 1976) and *A First Guide to Loss Prevention* (McCrindle,1981) and more substantial texts include *Industrial Safety Handbook* (Handley, 1977), *An Introduction to Loss Prevention* (Wells, 1980), *Industrial Hazard and Safety Handbook* (R. King and Magid, 1979), *Safety and Accident Prevention in Chemical Operations* (H.H. Fawcett and Wood, 1982), *High Risk Safety Technology* (A.E. Green, 1982b), *Major Chemical Hazards* (V.C. Marshall, 1987), *Chemical Process Safety* (Crowl and Louvar, 1990) and *Safety in the Process Industries* (R. King, 1990), as well as the present book.

A series of books by Kletz includes *Cheaper, Safer Plants* (Kletz, 1984d), *Learning from Accidents in Industry* (Kletz, 1988h), *What Went Wrong?* (Kletz, 1988n), *Improving Chemical Engineering Practices* (Kletz, 1990d), *An Engineer's View of Human Error* (Kletz, 1991e), *Plant Design for Safety* (Kletz, 1991g), *Hazop and Hazan* (Kletz, 1992b) and *Lessons from Disaster* (Kletz, 1993b).

The IChemE has been active in the production of a variety of aids. Table 27.5 lists a computer simulation, open learning modules, slide modules and video training modules on various topics. Other aids include the information exchange scheme of the *Loss Prevention Bulletin*, the publications listed in Appendix 28, and many of the books by Kletz just mentioned.

Another source of material is the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers (AIChE). Specifically educational material from this source includes *Safety Health and Loss Prevention in Chemical Processes: Problems for Undergraduate Engineering Curricula – Instructor's Guide* (CCPS, 1990).

There are available a number of films and videos, both on the process industries generally, and on safety and loss prevention in particular. Some of these are listed in Table 27.6.

27.19 Notation

Section 27.14

M_1, M_2, M_3	metrics
n_{hl}	number of hours lost
n_{lta}	number of lost time accidents
n_{ra}	number of reportable accidents
N_h	number of hours worked
N_p	number of persons at risk

Section 27.15

k	ratio defined by Equation [27.1.4]
n	size of population
P	probability
r	counter
x	observed number of events
μ	expected number of events
χ^2	chi-square

Subscripts:

1, 2	population 1, 2

28 Safety Systems

Contents

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Safety and loss prevention depend primarily on the overall management system, as described in Chapter 6 and also in other chapters. The people who carry the main responsibility for safety are the line managers rather than the safety specialists. At managerial as at other levels safety is everyone's responsibility. There remains a need, however, within the management system for a specific safety organization and for safety personnel. The quality of this safety system can have a significant effect on safety performance.

Selected references on process safety systems are given in Table 28.1.

Table 28.1 *Selected references on process safety systems (See also Tables 1.1, 6.1 and 27.1)*

ABCM (n.d./1, 1964/3); ILO (n.d.); Guelilch (1956); Simonds and Grimaldi (1963); H.H. Fawcett and Wood (1965); Sands and Bulkley (1967); CBI (1968); Leeah (1968); BCISC (1969/9, 1973/12); Handley (1969, 1977); Hearn (1969); Gilmore (1970); Freeman and Pickbourne (1971); Lloyd and Roberts (1971); R.L. Miller and Howard (1971); D. Petersen (1971–); D. Williams (1971); Kramers and Meijnen (1974); HSE (1975 HSW Bklt 35); Cocks and Rogerson (1978); W.G. Johnson (1980); Messing (1980); Kletz (1981l); Kilian (1982); London (1982); Willette (1982); Witter (1982); Tweeddale (1985 LPB 63); Harron (1986); Rausch (1986); E.K. Young (1986); McSween (1993)

Safety officers, safety advisers
Institution of Industrial Safety Officers (n.d.); ASSE (1966); J. Jones (1974); HSE (1976c); Kletz (1977g, 1982k); HSC (1983/2); Dawson, Poynter and Stevens (1985); D. Stevens (1986); D. Gray (1988); Hutcheon (1988)

Safety policy statement
BSC (n.d./8); CBI (1974); Egan (1975, 1979); HSC (1975 HSC 6, 1982 IAC/L1, 1991 HSC 6)

Trade unions and safety
M.J. White (1969, 1977); ILO (1971–72); Kinnersley (1973); Levinson (1975); TUC (1975); Cullen (1990)

Safety committees
HSC (HSC 8, 1977/3); RoSPA (IS/32); Ministry of Labour (1968)

Safety representatives
HSC (HSC 9, 1977/3); Egan (1978)

Safety training
Institution of Industrial Safety Officers (n.d.); BCISC (1965/5); Gimbel (1965b); Kingdon (1969); Atherton (1971); Burrage (1971); CAPITB (1971 Inf. Pap. 10, 1975 Inf, Pap. 16); PITB (1975/1–3); ILO (1980a); Kubias (1982); A.R. Hale (1984); D.J. Lewis (1984e); Roy (1984); FPA (1989 CFSD MR9); Bhoonchaisri (1990); J.R. Taylor (1993)

Organizational memory
Kletz (1980g, 1982j, 1985i, 1993c)

Communication
Tye (1969); D. Williams (1971); Lowe (1985)

Accident prevention
NSC (n.d./2, 1992/11); Devauchelle and Ney (1962); H.H. Fawcett and Wood (1965, 1982); McElroy (1965)

Proprietary systems
International Safety Rating System (ISRS): Bird and Germain (1985); Bond (1988 LPB 80); Eisner and Leger (1988); D. Petersen (1989); Pringle and Brown (1990); Arnold, Redfearn and Maaren (1992); Bird (1992 LPB 103)
MORT: W.G. Johnson (1977, 1980)

28.1 Safety Culture

It is crucial that senior management should give appropriate priority to safety and loss prevention. It is equally important that this attitude be shared by middle and junior management and by the workforce.

A positive attitude to safety, however, is not in itself sufficient to create a safety culture. Senior management needs to give leadership in quite specific ways. Safety publicity as such is often a relatively ineffective means of achieving this; attention to matters connected with safety appears tedious or even unmanly. A more fruitful approach is to emphasize safety and loss prevention as a matter of professionalism. This in fact is perhaps rather easier to do in the chemical industry, where there is a considerable technical content. The contribution of senior management, therefore, is to encourage professionalism in this area by assigning to it capable people, giving them appropriate objectives and resources, and creating proper systems of work. It is also important for it to respond to initiatives from below. The assignment of high priority to safety necessarily means that it is, and is known to be, a crucial factor in the assessment of the overall performance of management.

A fuller discussion of management leadership in creating a safety culture is given in Chapter 6.

28.2 Safety Organization

28.2.1 Safety department organization

It is normal for there to be a separate department responsible for safety and loss prevention. Titles vary, but generally include some combination of those two phrases.

Managers involved in safety work are generally referred to as safety managers, safety advisers or safety officers. The head of a larger department is typically designated as safety adviser and other staff as safety officers.

A large department may have staff who specialize in areas such as engineering, safety systems and manuals, training, and so on.

Other areas which may come within the safety department include occupational health and medical matters and environmental protection.

The safety department needs to be, and be seen to be, independent, and the organizational structure should

reflect this. In particular, the department should be independent of the production function.

28.2.2 Safety responsibilities

In broad terms, it is the responsibility of the safety organization to: participate in the formulation of safety policy; ensure that safety systems are created, maintained and adapted; ensure compliance with the regulatory requirements; review plants and procedures; identify, assess and monitor hazards; educate and train in safety; assist communication and promote feedback in safety matters; and contribute to technical developments in safety. Thus safety personnel are concerned with the development and maintenance of the overall safety system and with its application to particular works and to plants.

As already stated, it is line management which has the executive responsibility for safety, as it does for production; the role of the safety function is advisory. This means that in many areas of safety it is line management which undertakes an activity, but with assistance from the safety function. Accident investigation is a case in point.

In many instances, the safety department will monitor and will intervene only if necessary. For example, the plant emergency procedures manual should be revised periodically. The safety department will recognize a responsibility to see that this is done. If necessary, it will prompt line management to undertake the revision and may provide support.

Turning to the specific areas for which safety department typically takes some responsibility, these include

(1) advice to senior management, including –
  (a) overall safety policy,
  (b) safety management system,
  (c) compliance with regulatory requirements,
  (d) safety performance measurement,
  (e) technical aspects of safety,
  (f) safety cases;
(2) creation, monitoring and revision of safety management system, including –
  (a) personnel selection criteria,
  (b) process safety reviews, hazard studies,
  (c) safety auditing,
  (d) emergency planning,
  (e) accident investigation,
  (f) safety documentation,
  (g) safety training,
  (h) compliance with regulatory requirements;
(3) oversight and prompting of safety related activities, including those in (2);
(4) safety training, exercises and drills;
(5) communication, including –
  (a) developments in regulatory requirements,
  (b) developments in technology,
  (c) good practice in safety,
  (c) accident investigation and case histories.

The safety department has a responsibility to ensure that there exists a safety management system which is appropriate and comprehensive, to monitor its implementation and operation, and to undertake period audits and reviews and to make proposals for revision as necessary.

On safety matters the department should be the company's window on the outside world, monitoring developments, whether in legislation, technology or good practice.

For large projects the safety department will need to plan ahead in some detail, to ensure that the various process safety reviews and hazard studies are scheduled and resourced.

Increasingly, safety personnel are involved in technical matters. Typical areas where safety personnel have had a strong technical input in recent years include inherently safer design, trip systems, isolation arrangements, hazard identification techniques, hazard analysis, quantitative risk assessment and emergency planning.

The safety department will have a substantial commitment to education and training. This includes such essential aspects as: induction and refresher training on safety matters; and exercises and drills for emergencies such as a fire or toxic gas release and for fire fighting. But its activities should also go beyond this and should extend in two further directions in particular. One is the creation of the safety culture and the dissemination of good practice. The other is training for new safety-related techniques. Examples of techniques introduced in recent years are hazop studies and quantitative risk assessment. In both cases safety personnel have taken the lead in introducing the techniques and training engineers to apply the methods themselves. Safety training is considered further in Section 28.7.

Many of the activities described involve some form of communication. This is considered in more detail in Section 28.8.

28.2.3 Safety professionals

Personnel involved in work on safety and loss prevention tend to come from a variety of backgrounds and have a variety of qualifications and experience. It is possible, however, to identify certain trends. One is increasing professionalism. The appeal to professionalism is an essential part of the safety culture, and this must necessarily be reflected in the safety personnel. Another trend is the involvement in safety of engineers, particularly chemical engineers. A third trend is the extension of the influence of the safety professional.

Accounts of the safety professional, and his formation and accreditation, has been given by V.C. Marshall (1983a) and D.J. Lewis (1984e).

Many safety professionals are members of an engineering institution. The Institution of Chemical Engineers (IChemE) maintains a Register of Safety and Loss Prevention Specialists. For industry generally, the professional body for safety officers is the Institution of Industrial Safety Officers (IISO).

In the following section, an account is given of the role of a typical safety officer. Discussion of the role of the more senior safety adviser is deferred until Section 28.6.

28.2.4 Safety officer

The role of the safety officer is in most respects advisory. It is essential, however, for the safety officer to be influential and to have the technical competence and experience to be accepted by line management. The latter for their part are not likely persistently to disregard the advice of the safety officer if he possesses these

Table 28.2 *Safety specialist activities in relation to technical control of hazards (S. Dawson, Poynter and Stevens, 1985) (Reproduced by permission of Elsevier Science Publishers)*

	Stage of technical control				
Safety specialists' activities	*Identification of hazards*	*Assessment of risk*	*Development of controls*	*Implementation of controls*	*Longer term monitoring and adaptation*
A Processing information	Keeping accident statistics. Processing hazard information	Calculating accident frequencies, etc. Processing information on hygiene standards	Processing equipment manufacturers' information and lists of products, etc.	Processing orders for safety equipment	Comparing accident statistics over time
B Giving advice/ problem-solving					
B1 Passive adviser	Looking at work operations, on request. Investigating complaints	Answering questions about severity of hazards	Commenting on available controls which have been suggested	Commenting on effectiveness on request	Investigating accidents. Inspecting. Providing feedback on request
B2 Active adviser	Taking initiative in looking for hazards	Lobbying for appropriate standards, control limits	Recommending controls	Identifying shortfalls and improvements	Making recommendations for update/review of systems
C Taking direct executive action					
C1 Jointly with line management	Doing joint inspections and audits	Jointly deciding on standards	Jointly drawing up codes of practice	Joint supervision and approval or disapproval to jobs	Participating in reviews of arrangements
C2 Alone	Doing own inspections and audits	Deciding unilaterally what is safe/unsafe	Issuing instructions. Specifying controls to be followed	Supervising job. Exercising veto. Physically stopping people working	Modifying procedures, etc., on own initiative

qualifications and is seen to be supported by senior management.

The situation of the safety officer is one where there is a potential conflict between function and status. He may have to give unpopular advice to managers more senior than himself. It is a well understood principle of safety organization, however, that on certain matters function carries with it authority.

The safety officer should have direct access to a senior manager, e.g. works manager, should take advantage of this by regular meetings and should be seen to do so. This greatly strengthens the authority of the safety officer.

Much of the work of a safety officer is concerned with systems and procedures, with hazards and with technical matters. It should be emphasized, however, that the human side of the work is important. This is as true on major hazards plants as on others, since it is essential on such plants to ensure that there is high morale and that the systems and procedures are adhered to.

Although the safety officer's duties are mainly advisory, he may have certain line management functions such as responsibility for the fire fighting and security systems, and he or his assistants often have responsibilities in respect of the permit-to-work system.

28.2.5 Associated areas

Safety is commonly associated with one or both of two additional areas: (1) occupational health and (2) environmental protection.

The association of safety with occupational health is a long-standing one. In some cases the two have operated as separate, parallel functions, whilst in others one has been subsumed into the other. An account of the relationship between the two has been given by Kilian (1982). The increasingly strict requirements for industrial hygiene have resulted in a substantial expansion in occupational health which mirrors that in safety and loss prevention.

As environmental protection has grown in prominence, it has become increasingly linked with safety. There appear to be a number of reasons for this. One is that it may be a matter of chance whether an incident results in injury to people or in acute damage to the environment. Another is that the loss prevention approach is broadly applicable also to environmental protection. A third is

that it is often convenient to combine the safety and environmental functions.

28.2.6 Safety roles

A study of the role of safety specialists in industry from the viewpoint of the social scientist has been described by S. Dawson, Poynter and Stevens (1985).

They identify the three main activities of safety personnel as (1) processing and generating information, (2) giving advice and participating in problem-solving, and (3) taking direct action. These activities may be undertaken at any one of five stages of the technical control of hazards, namely (1) identification of hazards, (2) assessment of risk, (3) development of controls, (4) implementation of controls and (5) long-term monitoring and adaptation of risk and standards. They illustrate the matrix which arises from this schema, as shown in Table 28.2.

With regard to the sources of influence to which the safety specialist has access, the authors identify: (1) formal organizational position; (2) managerial dependence on specialist expertise; (3) patronage by senior management; (4) direct role in the control process; (5) internal coalitions, e.g. with the workforce; (6) external coalitions, e.g. with the Health and Safety Executive (HSE); and (7) personal qualities.

In respect of the dependence of senior management on safety specialists, they see the relationship extending from one in which the safety function is required to assure compliance and to deal with external agencies to one in which it has increasing relevance to core managerial objectives and activities.

28.3 Safety Policy Statement

The Health and Safety at Work etc. Act (HSWA) 1974, Section 2(3), states:

> Except in such cases as may be prescribed, it shall be the duty of every employer to prepare and as often as appropriate revise a written statement of his general policy with respect to the health and safety at work of his employees and the organization and arrangements for the time being in force for carrying out that policy, and to bring the statement and any revision of it to the notice of all his employees.

The Health and Safety Commission (HSC) (1975 HSC 6) has issued guidance notes on employers' policy statements.

No model policy statement has been issued. This is presumably because the provision of such a model statement would defeat one of the objectives, which is to oblige the employer to work out and explain his own particular approach.

It is suggested by the HSC, however, that in large or complex undertakings it may be appropriate to divide the policy statement into two parts. The first should be a single document giving a concise statement of general policy, organization and arrangements, and the second a more detailed document, or collection of documents, including manuals of rules and procedures.

28.4 Safety Representatives

A system of safety representatives with responsibility for their fellow workers at a particular workplace has long existed in chemical works. The HSWA 1974 makes formal provision for such safety representatives.

Section 2(4) of the Act provides for the appointment by recognized trade unions of safety representatives from amongst the employees; further reference to safety representatives is made in Sections 2(5)-2(7).

The Safety Representatives and Safety Committees Regulations 1977 implement this provision of the Act. The document *Safety Representatives and Safety Committees* (HSC, 1977/3) contains these regulations, the Approved Code of Practice (ACOP) on Safety Representatives and the guidance notes.

A safety representative is appointed by a trade union. He represents in the first instance the employees who are members of that union, but may by agreement represent other employees also. The functions of the safety representative are to represent the employees in consultation with the employer under Section 2(6) of the Act, which, the Regulations state

> Requires every employer to consult safety representatives with a view to the making and maintenance of arrangements which will enable him and his employees to co-operate effectively in promoting and developing measures to ensure the health and safety at work of the employees and in checking the effectiveness of such measures.

His specific functions are given in the Regulations as follows:

> (a) to investigate potential hazards and dangerous occurrences at the workplace (whether or not they are drawn to his attention by the employees he represents) and to examine the cause of accidents at the workplace;
> (b) to investigate complaints by any employee he represents relating to that employee's health, safety or welfare at work;
> (c) to make representations to the employer on matters arising out of sub-paragraphs (a) and (b) above;
> (d) to make representations to the employer on general matters affecting the health, safety or welfare at work of the employees at the workplace;
> (e) to carry out inspections in accordance with Regulation 5, 6 and 7 below;
> (f) to represent the employees he was appointed to represent in consultations at the workplace with inspectors of the Health and Safety Executive and of any other enforcing authority;
> (g) to receive information from inspectors in accordance with Section 28(8) of the 1974 Act;
> and
> (h) to attend meetings of safety committees where he attends in his capacity as a safety representative in connection with any of the above functions.

The safety representative should keep informed on the hazards of the workplace, the relevant legislation and the employer's safety policy, organization and arrangements.

The employer's duty to disclose information is particularly important in relation to safety representatives. The Regulations require an employer to make available to safety representatives information which is within the

employer's knowledge and which the representatives need to enable them to fulfil their function. The Regulations state:

> Safety representatives shall for the performance of their functions under Section 2(4) of the 1974 Act and under these Regulations, if they have given the employer reasonable notice, be entitled to inspect and take copies of any document relevant to the workplace or to the employees the safety representatives represent which the employer is required to keep by virtue of any relevant statutory provision within the meaning of Section 53(1) of the 1974 Act except a document consisting of or relating to any health record of an identifiable individual.

They continue:

> An employer shall make available to safety representatives the information within the employer's knowledge, necessary to enable them to fulfil their functions except
>
> (a) any information the disclosure of which would be against the interests of national security, or
> (b) any information which he could not disclose without contravening a prohibition imposed by or under an enactment, or
> (c) any information relating specifically to an individual, unless he has consented to its being disclosed, or
> (d) any information the disclosure of which would, for reasons other than its effect on health, safety or welfare at work, cause substantial injury to the employer's undertaking or, where the information was supplied to him by some other person, to the undertaking of that other person, or
> (e) any information obtained by the employer for the purpose of bringing, prosecuting or defending any legal proceedings.

The ACOP states that the information which the employer makes available should include:

> (a) information about the plans and performance of their undertaking and any changes proposed insofar as they affect the health and safety at work of their employees;
> (b) information of a technical nature about hazards to health and safety and precautions deemed necessary to eliminate or minimize them, in respect of machinery, plant, equipment, processes, systems of work and substances in use at work, including any relevant information provided by consultants or designers or by the manufacturer, importer or supplier of any article or substance used, or proposed to be used, at work by their employees;
> (c) information which the employer keeps relating to the occurrence of any accident, dangerous occurrence or notifiable industrial disease and any statistical records relating to such accidents, dangerous occurrences or cases of industrial notifiable disease;
> (d) any other information specifically related to matters affecting the health and safety at work of his employees, including the results or any measurements taken by the employer or persons acting on his behalf in the course of checking the effectiveness of his health and safety arrangements;
> (e) information on articles or substances which an employer issues to homeworkers.

Another important right of the safety representative is to inspect the workplace. The guidance notes refer to the following types of inspection:

> (a) safety tours – general inspections of the workplace;
> (b) safety sampling – systematic sampling of particular dangerous activities, processes or areas;
> (c) safety surveys – general inspections of the particular dangerous activities, processes or area.

The safety representative also has the right to carry out inspections following notifiable accidents, dangerous occurrences and notifiable industrial diseases.

The safety representative should act as a channel of communication between the management and the workforce on safety matters. The arrangements outlined create the conditions for a concerned individual to make a major contribution to the safety of his fellow workers.

The relation between safety representatives and safety committees is a flexible one. Safety representatives are not appointed by or responsible to safety committees, or vice versa. There are provisions to protect safety representatives from both civil and criminal legal action arising from the discharge of their duties.

28.5 Safety Committees

Feedback from works personnel on safety matters is often most effective through such informal channels as direct contact with a foreman or manager. The formal system consists of safety representatives and safety committees. The HSC document *Safety Representatives and Safety Committees* deals also with the latter.

The Regulations require the employer to establish a safety committee if requested to do so by at least two safety representatives. The guidance notes suggest that the objectives of a safety committee are to promote cooperation between employers and employees and to provide a forum for participation by employees in matters of health and safety and that specific functions might include:

> (a) the study of accident and notifiable diseases statistics and trends, so that reports can be made to management on unsafe and unhealthy conditions and practices, together with recommendations for corrective action;
> (b) examination of safety audit reports on a similar basis;
> (c) consideration of reports and factual information provided by inspectors of the enforcing authority under the Health and Safety at Work Act;
> (d) consideration of reports which safety representatives may wish to submit;
> (e) assistance in the development of works safety rules and safe systems of work;
> (f) a watch on the effectiveness of the safety content of employee training;
> (g) a watch on the adequacy of safety and health communication and publicity in the workplace;
> (h) the provision of a link with the appropriate inspectorates of the enforcing authority.

The existence of a safety committee does not in any way relieve management of its responsibility for safety, but such a committee can fulfil a valuable function in complementing the work of the professional safety personnel.

The response of management to suggestions made by the safety committee is very important. This does not mean that suggestions should always be accepted. But where they are not, a reasoned explanation should be given.

28.6 Safety Adviser

The safety department is led by safety adviser. The approach taken by the safety adviser may well have a crucial influence on safety and loss prevention in the company. In the process industries the work of the safety adviser is likely to have a large technical content. As loss prevention has grown in importance, so has the function of the safety adviser.

The role of the safety adviser is to a considerable extent what the person appointed makes of it. The approach taken by one safety adviser is illustrated by the work of Kletz, which is referred to frequently in this book. Some of the technological developments with which he is associated include: inherently safer design; hazop studies; hazard analysis, and the adoption of a quantitative approach generally; human factors; emergency isolation valves and trip systems; incident investigation; and safety education and training. Kletz has described his work in a number of books the titles of which are given in Chapter 27.

The work of other safety advisers mentioned in this book includes that of W.B. Howard (1983, 1984), Lynskey (1985) and Searson (1982, 1983).

28.7 Safety Training

Training in safety is important both for management and for workers. Some of the general principles which should govern such training are outlined in Chapter 14. The discussion here deals primarily with the content of training.

Guidance on safety training includes the BCISC's *Safety Training - A Guide for the Chemical Industry* (1965/5) and the CAPITB's *Safety Training* (1971 Inf. Pap. 10) and *Health and Safety at Work - Everyone's Concern* (1975 Inf. Pap. 16). Further accounts are given by Gimbel (1965b), Kingdon (1969), A.R. Hale (1984) and Roy (1984).

Managers require training, particularly in technical aspects of safety and in the loss prevention approach, in company systems and procedures, in the division of labour between the company's specialist safety personnel and themselves, and in training workers. Some topics in safety training for managers are listed in *Table 28.3.*

Any of the usual methods of training may be used, but particular mention should be made of case studies of incidents, which have proved especially effective. A number of case studies, often with audio-visual material have been produced by ICI and the IChemE. These include some of the case histories given in Appendix 1.

In addition, managers should also be familiar with the material which workers need to know. Workers require training particularly in recognition of hazards, in systems of work, in the use and location of safety equipment, and in actions to be taken in particular situations. Some topics in safety training for workers are listed in Table 28.4.

Table 28.3 *Some topics in safety training for managers*

Managerial responsibility for safety and loss prevention
Legal requirements, in particular the Health and Safety at Work etc. Act 1974, the Factories Act 1961, the CIMAH Regulations 1984 and the COSHH Regulations 1988 and the work of the Heatlh and Safety Executive
Principles of safety and loss prevention
Company's management system in relation to safety and loss prevention
Company safety policy, organization and arrangements, including safety personnel, safety representatives and safety committees
Hazards of the particular chemicals and processes
Accidents and accident prevention, including accident statistics and case studies
Pressure systems
Trip systems
Principle of independent assessment
Plant maintenance and modification procedures, including permits-to-work and authorization of modifications
Fire prevention and protection
Emergency planning arrangements
Training of personnel
Information feedback
Good housekeeping
Sources of information on safety and loss prevention, including both people and literature
Case histories

See also Table 28.4

For process operators the list given in Table 28.4 is complementary to that in Table 14.11, which covers more general aspects, but includes many which have a large safety content. In particular, aspects such as the identification of equipment are very important. Table 28.4 makes reference to various kinds of equipment such as those for personal protection, fire fighting, first aid and rescue. It is important that the training covers all aspects of its use, including when to use it, how to use it and where to find it.

Safety training should be included in the initial induction course so that the worker does not endanger himself and his fellows when he first goes onto the plant. Outline courses are given in the CAPITB's *Safety Training.*

This initial training should be supplemented as soon as possible by more thorough safety training.

The supervisor, or foreman, has a particularly important part to play in training workers.

Training needs to be supported by documentation of various kinds. The plant design and operating manuals are key documents for training. In particular, the use of task analysis to assist in the development of operating procedures and operating manuals has been described in Chapter 14 and the writing of operating manuals in Chapter 20.

There is a need also for documentation more specifically concerned with safety in aspects such as company safety rules and procedures, procedures in the case of fire and information on chemicals. Data sheets

Table 28.4 *Some topics in safety training for workers*

Workers' responsibility for safety
Legal background, in particular the Health and Safety at Work etc. Act 1974 and the Factories Act 1961
Company safety policy, organization and arrangements, in particular general safety rules, safety personnel, safety representatives and safety committees
Hazards of the particular chemicals and processes
Fire/explosion hazard (flammable mixture, ignition source). Ignition sources and precautions, including hazardous area classification, static electricity, welding, smoking. Fire spread, fire doors. Action on discovering fire or unignited leakage.
Toxic hazard. Action on discovering toxic release
Emergency arrangements, including alarm raising, alarm signals, escape routes, assembly points
Protective clothing, equipment use and location
Fire fighting methods, equipment use and location
Rescue methods, equipment use and location
First aid methods, equipment use and location
Lifting and handling
Permit and handover systems
Security, restricted areas
Good housekeeping
Accident reporting
Health, medical aspects
Case histories
See also Table 14.10

describing the properties and handling of individual chemicals are issued by various bodies.

Again case studies of incidents are an especially effective training technique. Atherton (1971) has described an interesting variation of this method in which the case study material consisting of slides and voice recordings was itself developed by a team comprising managers and workers. The incident selected for reconstruction was a real accident, in which a fitter removed a blank from a sulphuric acid line and received chemical burns. Extracts from the dialogue and points arising are shown in Table 28.5.

28.8 Safety Communication

A major aspect of the activity of safety personnel is communication in its various forms. This follows from the advisory role of the safety function. For the most part, communication takes place as a result of the participation of safety personnel in the various activities such as process safety reviews and hazard studies, emergency planning, safety training and safety cases. Such participation can be an effective means of creating and maintaining the safety culture.

In addition it should be one of the aims of the safety department to exploit a range of communication techniques to inform and motivate people at all levels in the organization. Matters on which it will wish to communicate include developments in regulatory requirements, developments in technology, and good practice in safety.

Table 28.5 *Extracts of dialogue from an accident case history reconstructed for training purposes (Atherton, 1971) (Courtesy of the Institution of Chemical Engineers)*

(a) Start of incident	
Dialogue	*Points arising*
Maintenance foreman: In the morning, Len, I want to put B2 pump in on the weak circulation tank in C.D.	1 Poor attitude by supervisor
Process foreman: O.K., George, I'll have a clearance ready for you. There's no need for me to be there, you know the job. I'll put a chalk mark on the flange where the blank has to be removed. Just tell the fitter to be careful but he'll know what he is doing.	2 Poor identification of equipment 3 Assumes the fitter knows the properties of the chemicals with which he will come into contact 4 No mention of any specific instructions 5 Question clearance procedure
(b) The fitter is about to remove the blank	
Dialogue	*Points arising*
Fitter: Right, can you pass me the $\frac{5}{8}$ in. spanner, Chris?	The man knows the correct procedure, but takes a short cut (a common theme of many accidents)
Apprentice: O.K.	
Fitter: I'll start on these back bolts first. By hell! These are tight.	
Apprentice: How long have these been in?	
Fitter: They look like originals, don't they?	
Apprentice: Aye.	
Fitter: I think we'll start on these front ones first, they look a bit easier.	

Table 28.6 *Some Questions I am Often Asked (after ICI Safety Newsletter)*

1	66/8	Do we spend more on safety than other companies?
2	67/4	Would two small plants be safer than one big one?
3	68/7	How can we change people's attitude to safety?
4	69/4	What is our policy on safety?
5	70/5	Men are unreliable so should we try to make out plants fully automatic?
6	71/9	Who should take the decisions on safety matters—the manager or the safety officer?
7	72/5	How can we keep alive the memory of incidents that have happened on the plant when the staff change every few years?
8	73/1	How will the new Health and Safety at Work Act affect us?
9	74/6	Is there any easy way to get people interested in the plant safety book?
10	75/6	How often will an operator act correctly when an alarm sounds?
11	76/6	Most of our checking will show nothing wrong—so what is our incentive to continue?
12	77/7	Why does the Petrochemical Division board issue so few directives on safety?
13	78/12	Can you recommend some books which will give me some background information on loss prevention
14	79/5	Are we expected to learn the lessons of accidents which have occurred somewhere else?
15	80/8	How long should a manager spend on a plant?
16	81/9	Why don't 'they' do more about safety (or plant tidiness or training)?
17	82/8	Do you put forward minimum standards? Can you go further than you suggest as long as you do not do less?
18	84/7	Flixborough has been described as the price of nylon—is it worth it?
19	85/6	How does our safety record compare with other companies?
20	86/4	In our designs, should we assume that people make mistakes?
21	87/5	What should we do to old plants when standards change?
22	88/6	How can I find out quickly and easily what has been written and recommended about subjects I am interested in at the moment?
23	91/8	Do we really need to do an operability study as this is only a very simple project (or it is very similar to the last one)?
24	92/6	What should we do to improve the safety record?
25	94/6	Are we willing to give information on safety to other companies?
26	95/5	Which airline should I fly?
27	96/5	What is the difference between operability studies and hazard analysis?
28	97/8	Is the Safety Newsletter issued free?
29	98/9	Do we spend too much money and effort on the problems that the press and TV publicize?
30	99/8	Can we get the money needed for safety?
31	100/6	What, in six words of one syllable, is the biggest single cause of accidents?
32	102/9	Can I be prosecuted if there is an accident on a plant which I work on or which I have designed?
33	108/7	What's new?
34	117/2	Does ICI add on more protective equipment than other companies?
35	119/5	How does ICI compare with other companies?
36	121/7	What should I do if a Factory Inspector asks me to do something which I think is unnecessary or even unsafe?
37	123/2	If we install a lot of automatic trips and controls on our plant, will we turn operators into zombies?
38	124/6	Has all the money and effort put into technical safety in the last 10 years produced any results?

There is a variety of techniques which are used to do this. There is commonly a safety newsletter. Table 28.6 shows some of the topics dealt with in issues of the ICI *Safety Newsletter*. Important features are that the topics are matters of concern and that the comments made are clear, practical, reasoned and authoritative.

Incident investigations and case histories, and the lessons drawn from these, provide concrete illustration of the principles. Incidents within the company are likely to make most impact, but it should be the case that these are not numerous enough to transmit the message, so that it is necessary to draw also on case histories from elsewhere. A detailed account of incident investigation and of the approach to drawing the lessons is given in Chapter 27.

The potential of case histories is not exhausted by recounting them in a newsletter. As described above, they should also be used in workshops, in which the group is invited to carry out its own analysis of the lessons to be learned and to formulate its own recommendations.

In addition to providing general reinforcement of the safety culture, such communication addresses two specific problems. One is raising the safety awareness of fresh and inexperienced personnel. Another is arresting the decay of procedures whose purpose is liable be forgotten if some time has elapsed since an incident occurred.

Another form of communication is to draw the attention of management to deterioration in the operation of systems and procedures and to malpractices. This is effective but requires a certain skill.

28.9 Safety Auditing

A major aspect of the work of the safety department is auditing. Audits are the periodic examination of the functioning of the safety system. Accounts of auditing are given in *Safety Auditing* (Kase and Wiese, 1990) and by D. Williams (1971), Madhavan and Sathe (1987), Madhavan and Kirsten (1988), Madhavan and Landry (1988), Monk (1988), Scheimann (1990), Tweeddale (1990a, 1993b), I.G. Wallace (1990), Galagher and

Table 28.7 *Some safety audit activities (after D. Williams, 1971) (Courtesy of the Institution of Chemical Engineers)*

Activity		*Interval* (month)
Plant safety review	Review of adequacy of operations, equipment and building safety	12
Job safety analysis	Reviews of standard operating procedures. Update where necessary	12
Operator review	Check for deviation from standard operating procedures and on work habits	6
Supervisors' safety meetings	Education, training, drills, follow-up	3
Management development seminar	Development of managerial competence	1
Supervisory training	Training of foremen for supervisory role	1
Safety committee	Motivational safety suggestions	1
Plant manager's meeting	Communication, education, training, innovation, follow-up	1
Foremen's meeting	Communication (vertical, horizontal), motivation, education, training	1
Critical incident technique	Observation of unsafe acts, conditions. Reports of near misses	1 Plus continuous observation
Central plant safety	Safety policy	As needed
Safety review committee	Review of safety of new processes and/or equipment	As needed
Works safety procedures review	Review of work safety procedures	As needed

Tweeddale (1992), Ozog and Stickles (1992), D. Scott and Crawley (1992), J. Lockwood (1993), Sankaran (1993), Hurst and Ratcliffe (1994) and Hurst, Hankin *et al.* (1994).

28.9.1 Types and time-scales of audit

The overall system of control and auditing needs to operate at three levels, which correspond to increasingly long time-scales:

Level	*Time-scale*
1	Monitoring of outputs of systems and procedures Short term, essentially continuous
2	Audit of implementation of systems and procedures Medium term
3	Audit of functioning and appropriateness of systems and procedures Long term

Subjects of audit at both Levels 2 and 3 should be (1) the safety management system of the company, (2) the safety management system and operation of the plant and (3) special features of the plant.

Some of the audit activities of a safety officer are shown in Table 28.7, which is adapted from a more detailed table on safety audits given by D. Williams (1971). Important points illustrated by this table are the involvement of management at all levels, the training of both management and workforce, and the role of systems and procedures.

28.9.2 Company audits

The overall safety management system of the company should be subject to audit. At Level 2 the audit should check that the systems established are being operated and at Level 3 that these systems are still appropriate.

28.9.3 Plant audits

At plant level, there should be a post-commissioning audit carried out soon after a plant has been commissioned. Audits should then repeated at intervals throughout the life of the plant. Plant audits should cover the safety management system of the plant, including operation, maintenance and control of change.

A structure for the conduct of the audit of a safety management system is available in the STATAS method described in Chapter 6.

28.9.4 Special feature audits

These general audits may be supplemented by audits in which some particular feature is examined in greater depth. Typical topics for such special feature audits might be the fire protection system or the permit-to-work system.

28.9.5 Audit aids

The conduct of a plant audit is assisted by the use of aids such as checklists.

One such aid is HAZCHECK and its developments, by Wells, Hurst and co-workers, which provide a structured set of checklists related to the root causes of accidents. This is described in Chapter 8.

The STATAS method utilizes question sets which have origins in this work and in that of Bellamy, Hurst and co-workers.

28.9.6 Audit procedure

The effectiveness of an audit is highly dependent on the technique used. There is some guidance available on these practical aspects of auditing.

Tweeddale (1990, 1993) describes an approach to the auditing of a typical management system, taking as an illustration the auditing of a procedure for maintenance work permits. He sets four questions, or hurdles:

(1) Do you have a procedure for . . . ?
(2) What are the main objectives of that procedure?
(3) How do you know whether that procedure is being properly applied in your area?
(4) Do you have to report to anyone about how well that procedure is being applied?

He shows how much these relatively simple questions can reveal.

28.9.7 Audit quality

Considerable effort is expended on audits in the process industries, but much of it is relatively ineffective in discovering defects in the systems examined. The quality of audit is crucial.

The point is illustrated by the audits conducted on Piper Alpha. Audits of various kinds were quite frequent, but none had picked up the numerous defects in the permit-to-work system. Yet once the Inquiry began, these defects were quickly laid bare in the evidence of the witness on this topic (Lockwood, 1989). This evidence repays study. The *Piper Alpha Report* is critical of the quality of the audits carried out.

28.10 Safety Rating

Some companies utilize as part of the safety system a safety rating system. Use may be made of a system developed in-house or of one of the proprietary systems. Three systems are described below - the ISRS, MORT and MANAGER systems - as illustrations of the types of system available.

A number of the accounts of audits referred to in Section 28.9 also contain rating schemes of various kinds.

28.10.1 Management and Oversight Risk Tree

One such system is the management and Oversight Risk Tree (MORT) described in *MORT Safety Assurance Systems* (W.G. Johnson, 1980). This system has been mentioned earlier in Chapters 2 and 27.

MORT provides a methodology for assessing a situation which may lead to an undesirable outcome such as injury or damage. The basic logic tree of MORT is shown in Figure 2.3. This MORT tree contains in structured form many of the basic concepts of safety management and engineering, including: the concepts of: vulnerable targets; harmful energy; precursor events; barriers to escalation; mitigation of consequences; management policy formulation; management policy implementation; and risk assessment.

28.10.2 International Safety Rating System

The International Safety Rating System was developed by Bird and co-workers at the International Loss Control Institute (ILCI) at Georgia State University. The philosophy underlying the system is given in *Practical Loss Control Leadership* (Bird and Germain, 1985). The evolution of the system has been described by Bond (1988 LPB 80).

Table 28.8 *Elements of International Safety Rating System*

1.	Leadership and administration
2.	Management training
3.	Planned inspections
4.	Job analysis and procedures
5.	Accident/incident investigation
6.	Planned job observation
7.	Emergency preparedness
8.	Organizational rules and regulations
9.	Accident/incident analysis
10.	Employee training
11.	Personal protective equipment
12.	Health control and services
13.	Programme evaluation system
14.	Purchasing and engineering control
15.	Personal communications
16.	Group meetings
17.	General promotion
18.	Hiring and placement
19.	Records and reports
20.	Off-the-job safety

The system developed as the Five Star Rating System, was refined jointly with the South African Chamber of Mines to yield the International Mining Safety Rating System, and was finally generalized to give the International Safety Rating System (ISRS). There are several versions of the system, including one for petrochemicals. The elements of the system are given in Table 28.8.

An account of the application of the system in a refinery has been given by Arnold, Redfearn and Maaren (1992) and of its application elsewhere by Eisner and Leger (1988) and Pringle and Brown (1990).

28.10.3 MANAGER system

The MANAGER system described by Pitblado, Williams and Slater (1990) and outlined in Chapter 9 was developed to assist in estimating the effect of the quality of management in quantitative risk assessment. A feature of the method is that it seeks to take account of all areas shown to be important in accident causation and of the incorporation of widely accepted management principles in all key elements of the safety management system.

28.10.4 Critique of rating systems

As mentioned in Chapter 6, a critique of safety rating, or packaged audit, systems has been given by D. Petersen (1989). He cites studies indicating that most packaged audit systems do not contain many of the elements found to be critical to safety performance and, on the other hand, that they do contain elements which fail to correlate with safety performance.

29 Computer Aids

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The use of computers in the design and control of process plants is now widespread. In addition to the group of applications which might now be regarded as conventional computer aided design, there are numerous other uses of computer aiding. The use of computer aided design and other computer aids is described in this chapter.

Accounts of computer aided design of process plants are given in *Computer-Aided Process Plant Design* (Leesley, 1982), *Foundations of Computer-Aided Process Design* (Westerberg and Chien, 1984), *Computational Methods for Process Simulation* (Ramirez, 1989), *Foundations of Computer-Aided Process Design* (Siirola, Grossman and Stephanopoulos, 1990) and *Computer-Aided Process Engineering* (Puigjaner and Espuna, 1991).

Reference has already been made in a number of chapters to various specialist computer codes such as those for human reliability assessment and software reliability assessment, and no further account of these is given here. Selected references on computer aided design and computer aids for process plants are given in Table 29.1.

A development in computer aiding which is now beginning to impinge on the process industries is the application of the techniques of artificial intelligence and, in particular, of expert systems. These are described in Chapter 30.

Table 29.1 *Selected references on computer aided design and computer aids in the process industries*

Computer aided design and engineering
ASME (1977/133, 1981/142, 1981 PVP 54, 1991/203, 1992/204); Peterson, Chen and Evans (1978); C. Davies (1979); Ryan (1979–); Westerberg *et al.* (1979); Angus and Winter (1981); Cherry *et al.* (1982); Fabian (1982a); Guy (1982a,b, 1983); Leesley (1982); Thomasson and Lebosse (1982); Winter, Branch and Smith (1982); Liles (1983); Proctor (1983); Anon (1984vv); Dunhill (1984a); Peters (1984, 1985); Petroulas and Reklaitis (1984); B. Turner (1984); AIChE (1985/81); Blaha, Yamashita and Motard (1985); Canfield (1985); Craft (1985); Salisbury (1985); Shelley (1985); Tayler (1985e); Winter (1985, 1986, 1992); Anon. (1986g); Baker-Counsell (1986a); Preece (1986, 1990); Atkinson (1987b, 1988b); Benayoune and Preece (1987); Holt *et al.* (1987); IMechE (1987/93, 1989/109, 1991/91); F. Knight (1987); Madden (1987); Preece *et al.* (1987); British Gas (1988 Comm. 1380); H. Evans (1988); Basta (1989); Berzins and Jones (1989); Biegler (1989); Rushton (1989); Sawyer (1989, 1991c); IChemE (1990/86); Siirola, Grossman and Stephanopoulos (1990); Fouhy (1991); Puigjaner and Espuna (1991); Sawyer (1991c, 1993a); Shearing (1991); Benson (1992); C. Butcher (1992a); Carell (1992); Gutermuth (1992); J.G.F. Shaw (1992); Shearman (1992); J. Turner (1992); Boston, Britt and Tayyabkhan (1993); Pekny (1993); Stadtherr, Cofer and Camarda (1993); Westerberg (1993); Horowitz (1994)
CEP Software Directory: CEP (1989, 1994)
CAD theory: Sargent and Westerberg (1964); Rudd (1968); Masso and Rudd (1969); Siirola, Powers and Rudd (1971a,b); R.W. Thompson and King (1972); Hendry, Rudd and Seider (1973); Soylemez and Seider (1973); Ramirez (1976, 1989); L.B. Evans, Joseph and Seider (1977); Stanley and Mah (1977); Westerberg *et al.* (1979); AIChE (1981/87, 1982/88, 1983/89); Nishida, Stephanopoulos and Westerberg (1981); Westerberg and Chien (1984); Mah (1990); Perregaard, Petersen and Gani (1992)
Autocad : Lubow (1987); Raker and Rice (1988); Schaefer and Brittain (1988)
Dynamic simulation: Dann and Henson (1978); Thambynayagam, Wood and Winter (1981); Guy (1983); Alcock (1985); Egol (1989b); Palas (1989); Pritchard (1989); Sawyer (1989, 1991b); Jarvis and Pantiledes (1991)
SPEEDUP: Sargent and Westerberg (1964); Sargent, Perkins and Thomas (1982); Pantelides (1988)

Legislation, compliance
Ohnishi (1980); Hughson (1992c)

Process plant design
PROCEDE: Preece and Stephens (1989)

Physical and chemical properties
Anon (1989d); Egol (1989)
CHEM-BANK: Silver Platter Information Services (1990a)
CHETAH: Frurip (1992)
Adiabatic flame temperature: Gordon and McBride (1971, 1976)

Health and safety
OSH-ROM: Roos (1984); Silver Platter Information Services (1990b)

Computational fluid dynamics (CFD)
ASME (Appendix 28 *Fluids Engineering*); Rosten and Spalding (n.d.); Harlow and Amsden (1971); Boris (1976); Boris and Book (1976); Hjertager (1982a,b); Bakke (1986b); Cross *et al.* (1989); Anon (1990f); C. Butcher (1991a); Swithenbank (1991); Hernandez and Crespo (1992); Dombrowski, Foumeny and Riza (1993); Foumeny and Benyahia (1993); CCPS (1994/15); Hjertager *et al.* (1994); Kandola and Morris (1994)

Materials of construction, corrosion
Baker-Counsell (1986a)

Plant layout
Armour, Buffa and Vollman (1964); R.C. Lee and Moore (1967); Seehof and Evans (1967); Gunn (1970); Bush and Wells (1972); Shocair (1978); Al-Asadi (1980); Madden, Pulford and Shadbolt (1990); Russo and Tortorella (1992)
PDMS: Leesley and Newell (1972); Newell (1974); Madden and Taylor (1979); D.J. Lawrence (1980); Leesley (1982); Baker-Counsell (1986d)
Visualization: Tani *et al.* (1992); Biach and Watt (1993)
Photogrammetry: S. Freeman (1985); Kenefick and Chirillo (1985); Tayler (1985a)

Plant equipment
Pressure vessels: Almon (1991)
Pumps: Hughson (1992b)
Piping: Hughson (1992a)

Plant utilities
Petroulas and Reklaitis (1984)

Pressure relief
Wai-Biu Cheng and Mah (1976); Crosby Valve and Gage (1994); Tanner (1994)

Reactor venting
SAFIRE: D.A. Shaw (1990); Friedel, Schecker and Wehmeier (1992)

Valve sequencing
Rivas and Rudd (1974); Rivas, Rudd and Kelly (1974)

Purge sequencing
Fusillo and Powers (1988a)

Fire protection
Cote (1990)
Water sprinkler hydraulics: Melley (1989); Ashfield (1993); Mowrer (1993); Jackman and Nolan (1994)

Reliability engineering (see also Table 29.5)
Brock and Cross (n.d.); Brock (1977); Davidson and Macdonald (1977); G.D.M. Pearson (1977); R.L. Williams (1977); Hastings and Jardine (1979); EPRI (1981b); Laviron, Carnino and Manaranche (1982); Attwood and Suitt (1983); Burnup (1986)

Hazard identification (see also Table 29.4)
Prugh (1992a); Neowhouse (1993)

Fault tree analysis (see also Tables 29.6 and 29.7)
Gateley, Stoddard and Williams (1968); Kongso (1970); Vesely and Narum (1970); Fussell, Henry and Marshall (1971); Semanderes (1971); Worrell (1974, 1985); Pande, Spector and Chatterjee (1975); van Slyke and Griffing (1975); Burdick, Marshall and Wilson (1976); Leverenz and Kirch (1976); Platz and Olsen (1976); Shaw and White (1976 SRD R57); Blin *et al.* (1977); Burdick *et al.* (1977); Cairns and Fleming (1977); Cate and Fussell (1977); Erdmann *et al.* (1977); Fussell *et al.* (1977). Goldberg and Vesely (1977); Lambert and Gilman (1977a,b); Matthews (1977); Olmos and Wolf (1977); Pelto and Purcell (1977); Vesely and Goldberg (1977a,b); Wheeler *et al.* (1977); Worrell and Stack (1977); Astolfi, Contini and van den Muyzenberg (1978); Erdmann, Leverenz and Kirch (1978); Erdmann *et al.* (1978); Gateley and Williams (1978); Rasmuson and Marshall (1978); Rasmuson *et al.* (1978); Rooney and Fussell (1978); Putney (1981); Contini, Silvestri and Cola (1983); Windebank (1983); Khan and Hunt (1989); Prugh (1992a)

Event tree analysis (see Table 29.8)

Escalation
Four Elements Ltd (1991)

Earthquake engineering
National Information Service for Earthquake Engineering (1982)

Hazard models
DECARA: Papazoglou *et al.* (1992)
CONSEQ: J. Singh and McBride (1990)

Emission
Drivas, Sabnis and Teuscher (1983)
Two-phase flow – HUBBLE-BUBBLE: Mather (1978 SRD R97); Martin (1978 SRD R118)
TRAUMA: Rutherford and Webber (1989 SRD R495); Webber and Brighton (1989 SRD R494)
BLOWDOWN: Haque, Richardson and Saville (1992)

Vaporization
Fenstermacher, Woodard and Adderson (1987)
GASP: Webber and Jones (1989 SRD R521); Webber (1990 SRD R507)
SPILL: Prince (1981 SRD R210)
SPILLS: Fleischer (1980)

Bund overflow
Phelps and Jureidini (1992)

Gas dispersion
Kaiser (1976 SRD R63); EPA (1977); Fryer and Kaiser (1978 SRD R134); McBride (1981); Ministry of Environment, Canada (1983); Balentine and Elgroth (1985); Computer Data Systems (1985); Havens and Spicer (1985); Oliverio *et al.* (1986); Paine *et al.* (1986); W.B. Petersen and Lavdas (1986); Raj (1986); Verholek (1986); Blewitt, Yohn and Ermak (1987); Fenstermacher, Woodard and Adderson (1987); Preston and Sinclair (1987); Puttock (1987b); Vigeant and Muzzola (1987); Riou (1988); Bais, Zerefos and Ziomas (1989); Egol (1989); Chaineau and Mavrothalassitis (1990); D.J. Wilson (1990); Schulze (1990); J. Singh and McBride (1990); Yoshikawa *et al.* (1990); Zannetti (1990); Goyal and Al-Jurashi (1991); Moser (1991)

Fires
Hagen and Milke (1994); Kandola and Morris (1994)
Building fires – FIRENET: Hall and Scattergood (1984 SRD R299)
Combustion – FLARE: Martin (1986 SRD R372, R373)
Pool fires – FIRE 2: Pritchard and Binding (1992)
Fire engulfment: Falck (1992); Meiers and Jarman (1993)
ENGULF: Ramskill (1983 SRD R241, 1987 SRD R413, R414, 1988, 1989 SRD 480); Ramskill and Hunt (1987 SRD R354); Ramskill and Marriott (1989 SRD R481); Duijm (1994)

Explosion, explosion simulation
Chong *et al.* (1993)
CLICHE: British Gas (1990); Catlin (1990)
EXSIM: CCPC (1994/15); Hjertager *et al.* (1994)
FLACS: Hjertager (1982); Bakke *et al.* (1989); Bakke, Bjerkevedt and Bjorkhaug (1990); CCPC (1994/15)
GASEX2: Mackenzie and Martin (1983 SRD R251); Martin (1983 SRD R173, R252)
REAGAS: van den Berg (1989); van den Berg, van Wingerden and The (1991)

Vapour cloud explosions
Chong *et al.* (1993)
BLAST, CLOUD: Zeeuwen (1982)
CMBWAT: Madsen and Wagner (1994)

Explosion damage
Briscoe (1979 SRD R155)

Toxic releases
Touma and Stroupe (1991); D.J. Wilson (1991b)

Hazard assessment systems
Holton, Baker and Casada (1987); Egol (1989); Merz and Halbritter (1989); Pitblado and Nalpanis (1989); Raj (1990); J.L. Woodward (1990); Marnicio *et al.* (1991); Barbieri *et al.* (1992); Stead (1992); Worthington (1992)
HSE codes, Riskat: Pape and Nussey (1985); Crossthwaite, Fitzpatrick and Hurst (1988); Hurst, Nussey and Pape (1989); Nussey, Pantony and Smallwood (1992)
ARCHIE: FEMA (1989); Early, Livingston and Newsom (1990)
CHAOS: British Gas (*c.* 1991 Comm. 1493)
DYLAM: Labath and Amendola (1989)
SAFETI: Beevers (1985a); Ale and Whitehouse (1986); N.C. Harris (1986); Pitblado and Nalpanis (1989)
TRANSPIRE: Hopkins (1993); Hopkins, Lewis and Ramage (1993)
WHAZAN: World Bank, Office of Environmental and Scientific Affairs (1985)

Process control (see Table 13.3)

Performance and condition monitoring
Whillier (1967); Ridenhour (1982)

Alarm design, display and diagnosis
Finch and Kramer (1988); Bossche (1991c)

Maintenance
Hughson (1991b)

Emergency planning and response
Hesel and Schnadt (1982); Lashover (1985); Stern (1986); Egol (1989); McPherson (1989); Hughson (1991a); R.A. Freeman and Shaw (1992); Preston (1993, 1994)
CHARM: Columbia Scientific Industries (1990)
SAFER: Safer Emergency Systems Inc (n.d.); Anon (1982e,g); Gelinas (1985); Hughson (1991a)
Transport emergencies: Raj (1990)

Incident, failure and event data banks (see Tables A1.1, A14.1)

Occupational health
C.W. Ross (1984)

Engineer's responsibility for computer-based decisions
IChemE (1987a)

29.1 Responsibility for Computer Aids

The engineer has a responsibility to ensure that the use of computer programs is not the source of errors and incidents. Guidance on this is given in *The Engineer's Responsibility for Computer Based Decisions* by the IChemE (1987) (the IChemE *Computer Based Decisions Guide*). This document deals essentially with computer aids used as decision tools. It does not address computer aided drafting and three-dimensional modelling of plant. Some categories of computer aid and typical sources of error in their use are given in Table 29.2.

29.1.1 Legal responsibility of engineers

Under Section 6 of the Health and Safety at Work etc. Act 1974 (HSWA) a legal responsibility attaches to an article for use at work, as described in Chapter 3. It must be so designed and constructed as to be safe, it must be adequately tested, and adequate information must be provided about it. Section 7 on the duty of care is also relevant.

The employer of the designer of software has a vicarious liability for injury arising from defects in it. Such an action may be defended by showing that good software engineering practices, including testing, have been used in the design of the software.

Likewise, there is a corresponding liability on the employer of the user of software. An action may be defended by showing that good practice has been followed in checking the software for the use to which it is put.

The *Guide* contains an appendix giving further guidance.

29.1.2 Guidance for engineers

The *Guide* gives guidance for four categories of person: (a) academics, (b) engineering managers, (c) engineers, and (d) software developers. The guidance to academics relates to the teaching of engineers.

The engineering manager should ensure that the engineer involved is competent in the engineering problem, not merely in the software, and thus able to assess properly the results obtained. The extent of manual checking should relate to the experience of the engineer. If the results are accepted on the basis of judgment, this should be real and relevant. The programs used for design should be subject to quality control with a proper process of selection and testing. The engineer can be asked to justify the use of a particular program and the input data set for a particular problem. Caution should be exercised in the use of relatively untried programs, particularly those written in house. The program should have adequate warning and diagnostic facilities. When errors or failures occur, in initial testing or in use, records should be kept of the circumstances. Results used in design should be properly written up, with a statement of the problem and an interpretation of the results. It is not enough simply to file the raw output.

The engineer should familiarize himself with the models and methods of solution used and with the program documentation and should appreciate their limitations. He should review the results and seek to assess their accuracy and sensitivity, adopting a sceptical approach to both the software and the input data.

The software developer should follow good software engineering practice and should have a system of quality control. The user interface should be designed to maintain consistency, avoiding omission of units, mixtures of units and unannounced changes in orders of magnitude. The program should contain a battery of checks, including checks on the input data and on

Table 29.2 *Some common sources of error in the computer aided design of process plants (IChemE, 1987a reproduced by permission of the Institution of Chemical Engineers)*

	Databanks	*Calculation programs*	*Design checking*	*Data management*	*PC software*	*Expert systems*
Incorrect input data	*	*	*	*	*	*
Invalid algorithm		*				
Invalid use of an algorithm		*				
Invalid coding of design rules			*			*
Design rules wrong, ambiguous or conflicting			*			*
Incorrect data stored	*		*	*		
Correct data incorrectly stored			*	*		
Data being incorrectly selected	*	*		*		
Data being wrongly interpreted or applied	*	*		*		*
Transcription errors	*			*		
Spreadsheet formulae incorrect					*	
Expertise (knowledge) wrong			*			*
Expertise wrongly coded			*			*
Incorrect problem data supplied			*			*
Inference wrongly deduced			*			*

intermediate values generated during the calculations. The output should contain enough explanation and data to identify the particular problem, to distinguish between data supplied and default values and to allow the results to be checked. Such checking is assisted by the output of intermediate results also. The developer should give information on the solution methods to assist the user to assess their suitability for his purposes, to estimate the accuracy and reliability of the results and, where possible, to perform manual checks.

29.1.3 Sources of error

Common sources of error are shown in Table 29.2. Incorrect input data occur not only due to simple input errors, but also due to the use of incorrect units and confusion between items of data induced by the input format. An algorithm may be invalid for some of combinations of data permitted by the program and it may be used outside its range of applicability. Design rules may be incorrectly coded or may be incorrect, ambiguous or conflicting in the first place. Stored data may have an incorrect value, may be incorrectly labelled in, or incorrectly retrieved from, the store. There are various errors which can arise in the use of spreadsheets, often due to the fact that the formulae are normally invisible.

Where an expert system is used, the encoding of the expertise is prone to various forms of error. It is not uncommon for logical expressions to be wrongly coded. Less formal expertise gives appreciable scope for error. Requests by the program for input data may not be effective in eliciting correct data. Incorrect deduction of inferences is a less common source of error.

29.2 Chemical Engineering Software

29.2.1 Some software suppliers

Suppliers of software of particular relevance in the present context include:

AAA Technology
AEA Technology
AKC Technology
American Institute of Chemical Engineers (AIChE) and the Center for Chemical Process Safety (CCPS)
Applications Development
Applicon
ASA
Aspen Technology
Autodeck
Autotrol
WS Atkins
British Gas
John Brown
CADCentre
Cambridge Scientific Computing
Certech
CFD Services
Chemical Engineering Software and Services (CESS)
Chemical Information Systems (CIS)
Cherwell Scien
Computervision
Davy
Deerhaven Technical Software
DIPPR
DnV
DnV Technica
Dow Chemical Co.
Dupont
Dynacomp
Engineering Design Automation (EDA)
Engineering Software
Four Elements
Gardner Process Operations (GPO)
Gulf Publishing
Hazmat America
Heat Transfer Research (HTR)
Hypertech
IChemE

ICI
Instrument Society of America (ISA)
Intergraph
International Atomic Energy Agency (IAEA)
International Software Systems (ISS)
JBF Associates
AD Little
National Institute of Standards and Technology (NIST)
OSHA-Soft
OREDA
Pafec
Pickard, Lowe and Garrick (PLG)
Primatech
Silver Platter
Simulation Sciences (Simsci)
STN International
Techdata
Technical Database Services (TDS)
Tecs Software
Tees Engineering
Thermal Analysis Systems (TAS)
Thermodynamics Research Center (TRC)
Toegepast-Natuurwetenschappelijk Onderzoek (TNO)
Trinity Consultants
University College, London (UCL)
Whessoe

The addresses of most of the above are given in the CEP *Software Directory* described below.

29.2.2 Some software series

Many programs are parts of a series issued by the particular supplier. Some principal series are:

AutoPLANT *program*	Engineering Design Consultants
BREEZE	Trinity consultants
CADPIPE *program*	International Software Systems
*program*CALC	Gulf
program-FLO	Engineering Software
GAS*program*	Gardner Process Operations
Hy*program*	Hypertech
NIST*program*	National Institute of Standards and Technology
OMNI*program*	Applications Development
program-PC	Primatech
PDP*program*	Deerhaven
PRO*program*	Applications Development
T*program*	Tees Engineering
TMA-program	Gulf
TRC *program*	Thermodynamics Research Center
TRI *program*	AAA Technology

where *program* denotes the remainder of the title of the individual program.

29.2.3 CEP *Software Directory*

An annotated listing of programs relevant to chemical engineering is issued annually by *Chemical Engineering Progress* (CEP) in the form of a software directory. The listing constitutes the authors' best endeavours in a rapidly changing field, but makes no claim to completeness. The programs are principally North American with some for the UK, but little representation for other sources.

The 1994 CEP *Software Directory* (CEP, 1994) lists some 1700 programs from over 520 vendors. Of the programs listed, 400 are new whilst 300 have dropped out of the list, making a net increase of 100 programs over the previous year and indicating a high turnover. It gives for each program a brief description, including the number of years it has been available and details of the computing platform required.

29.3 Computer Aided Design and Engineering

There are now a large number of computer aids for the design and operation of process plants. Reference has already been made to various aspects of computer aiding in the preceding chapters. Here an overview is given of the use of computer aids, and some of the principal packages are briefly described.

The practice of computer aided design (CAD), or computer aided design and engineering (CADE), should involve more than the utilization of a number of individual computer codes. CAD provides the means of putting the whole design environment on a more rational and systematic basis, and unless this potential is exploited the full benefits will not be obtained.

The main elements of conventional CAD of interest in the present context are the design of the overall process and of the unit operations, the mechanical design of vessels and pipework, and the design of the plant layout. The use of computers for many of these aspects of the design is now widespread.

There are a number of companies which offer integrated CAD packages for process and plant design. Often these come as turnkey systems in which the supplier provides not only the computer programs but also the machine on which they run.

The process industries also make use CAD systems developed for other industries. This is true particularly of sophisticated graphics packages.

The development of computer aids specifically for loss prevention aspects such as hazard identification and assessment, alarm handling and emergency planning is less advanced but is now occurring rapidly.

29.3.1 Graphics systems

General purpose graphics systems play an important part in CAD. Many of these have been developed for engineering applications other than those of the process industries. They include some extremely power graphics tools.

Some general purpose graphics packages include:

Autocad (Autodeck)
BRAVO (Applicon)
ChemOffice (CSC)
DOGS (Pafec)
Series 5000 (Autotrol)

Packages such as DOGS and Autocad are two-dimensional drafting tools which may be used for a wide variety of process applications, including piping and instrument diagrams. Various organizations have developed complementary packages, such as sets of process engineering symbols, for such applications.

Guidance on instrument symbols is given in the program Library of Standard Symbols (ISA).

29.4 Computer Aided Process Engineering

Some of the principle codes for process plant design in CAD, or computer aided process engineering (CAPE), are now reviewed, considering first individual programs and then integrated packages.

29.4.1 Process selection

The selection of the process is perhaps the most fundamental problem in process design and it is a tough one. An account of the developments in the computer aiding of process route selection is given in Chapter 30.

29.4.2 Physical, thermodynamic and phase equilibrium properties

A package which furnishes physical, thermodynamic and vapour–liquid equilibrium properties is an essential service package for process design. Some of the packages are part of a suite of programs, typically supporting a flowsheet simulator. Some principal packages for such data include:

CHEMCALC 7 (Gulf)
CHEMCO (CESS)
CHEMSAFE (TDS)
CHEMTRAN (Chemshare)
DIPPR (AIChE) (also STN, NIST)
HYPROP (Hypertech)
KEYDATA (CADCentre)
MIXDAT (Chemshare)
PHYSPAC (ICI)
PPDS (IChemE)
PROPERTIES-PLUS (Aspen Technology)
TAPP (ES Microware)
Thermodynamic and Physical Property Data (Gulf)
VLE (AIChE)

There is also the TRC series of the Thermodynamics Research Center.

Programs for steam tables include:

Steam Tables (Gulf)
STEAMPAK (Cryodata)
Thermodynamic Properties of Water and Steam (ISA)
TSTEAM (Tees Engineering)

Properties of heat transfer fluids are given in:

PROPHT/SELECT (TDS)

29.4.3 Flowsheet simulation

Flowsheet simulation, handling the mass and energy balances, is the heart of the process design package. Much theoretical work has been done to produce codes which are efficient, particularly in handling features such as recycles. Some principal flowsheet simulation balance programs include:

ASPEN PLUS (Aspen Technology)
DESIGN II (Chemshare)
FLOWPACK II (ICI)
FLOWTRAN (Monsanto)
GENESIS (BP)
METSIM (metallurgical processes) (Mathew Hall Ortech)
PROCESS (ScimSci)
SPEEDUP (Prosys/Aspen Technology)
SYMBOL (CADCentre)
UNIOPT (CESS)

29.4.4 Piping and instrument diagrams

Closely linked to the flowsheet simulation is the generation of the process flow diagram (PFD) or piping and instrument diagram (P&ID). Some programs which handle this aspect are:

AutoPLANT P&ID (EDA)
CADPIPE P&ID (ISS)
OMNI-FLOW (Applications Development)
P&ID (Intergraph)
PRO-FLOW (Applications Development)

29.4.5 Process synthesis

Closely linked to the mass and energy balances is the thermal economy. Programs for heat exchanger network design and for process synthesis using pinch technology include:

ADVENT (Aspen Technology)
CHEMCALC 5 (Gulf)
HEATNET (NEL)
HEXNET (Profimatics)
Supertarget (Linhoff March)
SYNSET (CESS)

29.4.6 Cost and economic estimates

Another essential service package is a program which furnishes cost data and can be used to estimate the costs of designs. Some cost and economic packages include:

ECONOMIST (CADCentre)
NEWCOST (ICI)

29.4.7 Project engineering

A complete process and mechanical design system requires a package which integrates the other individual packages. Typically this system combines a flexible data base with a two-dimensional graphics facility. Some two-dimensional programs of this type include:

PEGS (CADCentre)
DRAGON (CADCentre)
PROVUE DB/PROVUE 2D (ICI)

Some three-dimensional programs include:

PDMS (CADCentre)
PROVUE 3D (ICI)

29.4.8 Engineering design workbenches and environments

PROCEDE (Cherwell) is an engineering design environment package for the production of engineering drawings, reports, etc. It includes the programs FLOSHEET 3 for engineering sketches and full engineering drawings, SPECSHT for design data management, and SYMGEN for equipment symbol configuration and management. An account of PROCEDE is given by Preece and Stephens (1989).

Another such package is Engineers Aid (EPCON), which possesses a variety of facilities for sizing pipework, pumps and fans, control and relief valves, heat exchangers, etc., combined with project management and specification writing and with the DIPPR database.

A third package is PEW (Process Engineer's Workbench) (CESS).

29.4.9 Engineering units conversion aids

Aids for conversion between different chemical engineering units include the Process Engineer's Conversion Kit (Dynacomp).

29.5 Project and Production Management

There are available a number of programs for project and production management. These include in particular programs to support (1) production planning and scheduling, (2) batch processing, (3) maintenance management, (4) document production and management and (5) work study.

29.6 Pipework

29.6.1 Fluid flow

Programs for pipework are of several different types. One group performs the fluid flow calculations for piping and piping networks. Programs of this type include:

CHEMCALC 2 (Gulf)
FLOW (F37) (Certech)
HYDRONET (Engineered Software)
NET-FLO (Engineered Software)
PIPECALC (Dynacomp)
PIPECALC 1 (Gulf)
PIPE-FLO (Engineered Software)
PIPENET Standard Module (Sunrise Systems, CADCentre)
PIPE-PRO (PDE)
TNET (Tees Engineering)
TPIPE (Tees Engineering)
TRIFLOW (AAA Technology)

29.6.2 Two-phase flow

This category of program includes those dealing with two-phase flow, such as:

CHEMCALC 4 (Gulf)
MULTIFLOW II (Kelix Software Systems)
Multiphase and General Fluid Flow (Dynacomp)
PIPE-PRO (PDE)
PIPESIZE (F38) (Certech)
TWO-PHASE (Dynacomp)
TWOPHASE (AKC Technology)

29.6.3 Flash-off and flash drums

Programs for flash-off and flash drums include:

CHEMCALC 1 and 10 (Gulf)
CSPACK (Tecs Software)
MADD-1 (Gulf)
PDP-FLASH (Deerhaven)
PRPACK (Tecs Software)

29.6.4 Unsteady-state flow

Another category of flow calculation is unsteady-state flow, which is treated in programs such as PIPENET Transient Module (Sunrise Systems).

29.6.5 Flow through control valves

Programs are available for the calculation of flow through control valves, such as:

CON-FLO (Engineered Software)
CONTROL VALVE SIZING FLUID CONTROL ANALYSIS (Dynacomp)
INSTRUCALC (Dynacomp)

29.6.6 Flow through rotating machinery

Programs are also available to calculate the flow through rotating machinery. They include:

CHEMCALC 8 (Gulf) Pumps
CHEMCALC 15 (Gulf) Compressors
PUMP-FLO (Engineered Software) Pumps

29.6.7 Pipe routing

A third group of programs handle pipe routing. Included here is PIPER (CADCentre).

29.6.8 Piping orthographics and isometrics

The fourth group produce piping orthographics and isometrics. In this category are:

AutoPLANT Isogen (EDA)
AutoPLANT Isometrics (EDA)
CADPIPE ISO (ISS)
CADPIPE ORTHO (ISS)
ISOGEN (ICI)
OMNI-ISO (Applications Development)
PRO-ISO (Applications Development)

29.6.9 Mechanical design

Another group deal with the mechanical design of the actual pipework. In this group are the programs:

PSA5 (Whessoe)
TRIFLANGE (AAA Technology)
TRIFLEX (AAA Technology, CADCentre)

29.6.10 Specialist topics

A fifth group deal with special problems in piping systems. They include:

AIRFLOW (Dynacomp) HVAC systems
Gravity Drain Flow (Thermal Analysis Systems) Drainage of liquid from pipes
HYPSMOS (BHRA) Pressure surge analysis
PIG (Techdata) Passage of a pig
PIPENET Spray/Sprinkler Module (Sunrise Systems) Sprinkler systems

29.6.11 Piping system management

A sixth group handle piping system management. They include:

COMDACE (John Brown)
OMNI-PIPE (Applications Development)
PIPE-FLO (Engineered Software)
PRO-PIPE (Applications Development)

The COMDACE package provides an integrated system for the management of piping systems from design to construction. It includes: COMPIPE for the management of piping specifications, materials take-off, etc.;

COMPROC for piping procurements; and COMSITE for materials control on site.

29.6.12 Pipelines

Programs for pipelines may be regarded as a separate category from those for pipework. This class includes PIPEPHASE (Scimsci).

29.7 Unit Operation and Equipment

29.7.1 Heat exchangers

There are a number of programs for the design of heat exchangers of various types. Programs exist not just for shell and tube heat exchangers but also for air-cooled heat exchangers, thermosyphon reboilers, furnaces, etc.

Some programs for heat exchanger design include:

CHEMCALC 6 (Gulf)
HEATEX (CESS)
HETEX (University of Tulsa)
HEXNET (Profimatics)
TRI*THERM (AAA Technology)

together with the program suites

DACE, PIPE, SCON, STEP, TREB, etc. (HTFS)
CST-1, RKH-2, RTF-2, ST-5 (HTR)
TMA, TMA-Air Cooler, TME-MECH, TMA-THERM (Gulf)

There are also programs for heat exchanger networks, as described in Section 29.4.

29.7.2 Chemical reactors

Programs for chemical reactor design include:

BATCHCAD (Chemstations) Batch and continuous
PHENICS (AM Associates) Steam crackers
REACTION (Batchcad) Batch and continuous
REACTSET (CESS) Batch and continuous
VESSELPAK (Madison Technical Software) Jacketed vessel heat transfer

29.7.3 Distillation columns

The design of distillation columns is well served by programs. They include:

BATCHDIST (CESS)
BATCHFRAC (Aspen Technology)
DISTILSET (CESS)
FRACHEM (ChemSolve)
INTERN (CESS)
MADCAP (SACDA)
MADD-2, 3 and 4 (Gulf)
MULTICOL (CADCentre)
PDP-DIST (Deerhaven)
RADFRAC (Aspen Technology)
RATEFRAC (Aspen Technology)
MULTIFRAC (Aspen Technology)
SP-10 (SimSci)
TOWER (AKC Technology)

29.7.4 Fired heaters

Programs for fired heaters include:

FH-O (HTR)
Fired Heater (Information Resource Consultants)
HEATER (University of Tulsa)
TBRUN (Tees Engineering)

29.7.5 Other unit operations

Some programs for other unit operations include:

ADSIM/SU (Aspen Technology) Adsorption
ADSORB (Svedberg) Adsorption
CEDA (University of Houston) Air pollution equipment
EVAP (SACDA) Evaporators
SEPARATE (Tecs Software) Separators
STIRRER (CESS) Stirred tanks
Z ABSORBER (Certech) Absorption

29.7.6 Equipment selection

Aids for equipment selection include:

Equipment Selection in Solid–Liquid Separation Expert System (Fine Particle Software)
PC-SELECT (Separation Technology Associates) Solid–liquid separation

29.7.7 Flare systems

Programs for flare systems include:

CHEMCALC 12 (Gulf)
FLARE (Techdata)
FLARE (F34) (Certech)
FLAREHDR (Tecs Software)
FLARENET (Hyprotech)
FLARESIM (Hyprotech)
FLARESTK (Tecs Software)
SUPERFLARE (UCL)

29.7.8 Steam systems

Programs for steam systems are represented by:

MOD ES1 (Techdata)
STEAM (F36) (Certech)
Steam Needs Analysis Program (Spirax-Sarco)
STEAMBAC C (PPS Systems)
STEAMSYS (Aspen Technology)
TRI STEAM (AAA Technology, CADCentre)

29.7.9 Pumps and compressors

Programs for pumps include:

COMPUMP (Tecs Software)
Gas Compressor (Thermal Analysis Systems)
TPCMPR (Tees Engineering)

and for compressors

COMPRESS (Codeware)
COMPUMP (Tecs Software)
EQUIP (AKC Technology)
PDP-COMP (Deerhaven)
PUMP (Techdata)
PUMP-FLO (Engineered Software)
TPUMP (Tees Engineering)

29.7.10 Heat transfer coefficients

In addition, programs are available for the calculation of particular features of process equipment. For example, representative of programs for heat transfer coefficients are the codes:

CHEMCALC 3 (Gulf)
Convective Heat Transfer (Dynacomp)

29.8 Mechanical Design

29.8.1 Vessels and tanks

Programs for the mechanical design of vessels include:

ASME8 (CADCentre)
DELOS (Whessoe) Storage tanks
PVE5 (Whessoe)
SPADE (Whessoe) Storage spheres
TANK (CADCentre)
TRI-FLANGE (AAA Technology)
TRI-VESSEL (AAA Technology)
VESSEL (Tecs Software)
VESSEL (F19) (Certech)
VESSEL 55 (CADCentre)
WERCO (AAA Technology, CADCentre)

29.8.2 Heat exchangers

Programs for mechanical design of heat exchangers include:

CHEMCALC 6 (Gulf)
HED5 (Whessoe)
STEM (CADCentre)

29.8.3 Ancillaries and utilities

There are also programs for ancillaries and utilities, including TraceCalc (Raychem) for trace heating.

29.9 Integrated Systems

The main suppliers of CAD software for process plant design offer systems which coordinate the individual packages and provide to varying degrees an integrated system. Some principal suppliers of integrated CAD systems for process and plant design are:

Applicon
Aspen Technology
Autotrol
CADCentre
Chemshare
Computervision
Hyprotech
Integraph
Simsci

In many cases the supplier's package is a turnkey system which includes not only the software but also the hardware to support it.

29.9.1 Process simulators

The core of a CAD system for process plant design is the program which performs the steady-state mass and heat balances, often called the process simulator. There are two main types of process simulator. The sequential modular (SM) simulator consists of a sequence of modules for the various unit operations performed. A basic set of modules is a mixer, a divider and a reactor. The equations of each unit operation are solved sequentially. The equation oriented (EO) simulator, by contrast, solves the equations of the whole system simultaneously. An SM simulator can accommodate more readily a variety of types of model in the modules, including user configured models, whereas the EO simulator scores for features which span a number of units such as recycles, control systems and constraints. The process simulator forms the core of an integrated CAPE system.

29.9.2 Other facilities

This core program draws on programs offering other facilities. These include physical properties, equipment sizing, cost and economics, and dynamic simulation packages.

29.9.3 Databases

An important feature of a fully integrated CAPE system is the database. The database may contain files on a wide variety of aspects of the design, from flows, pressures and temperatures to material take-offs. Database packages include:

CADPIPE INTERact (ISS)
ChemEng DB (CESS)
PRODOBAS (Prosys, Aspen Technology)
PROVUE DB (ICI)

It is understood that PRODOBAS is no longer supported.

29.9.4 Degree of integration

Different CAPE systems start from different starting points. One may start from a graphics facility, another from a process simulator. Consequently, the systems have different strengths and weaknesses.

The degree of integration in current CAPE systems is not always as advanced as might be assumed. Typically a two-dimensional package will have its own database which allows it to draw symbols representing plant units, but it does not identify the symbols as units such as vessels or heat exchangers, and does not have associated information about the units. In other words, it is purely a drawing package. This means that it cannot readily be used to capture the data about the units required for a package to perform a function such as fault tree synthesis.

29.9.5 ASPEN system

The facilities available in a CAPE system based on a process simulator may be illustrated by reference to the Aspen system based on ASPEN-PLUS. This system contains, among other things: several physical property databases, including DIPPR; a wide range of models for physical and thermodynamic properties; a large library of models for reactors, distillation columns and other unit operations such as BATCHFRAC; the dynamic simulator SPEEDUP; and process optimization and economic evaluation programs.

The system contains the program Model Manager which allows it to be integrated with other commercial systems such as: properties databases; database systems; graphics systems such as those of Autocad and Intergraph; synthesis tools such as ADVENT; process design programs for columns and heat exchangers; and facilities such as spreadsheets.

A PC flowsheet simulator system, MAX, is also available.

29.9.6 Hyprotech system
Another integrated system is the Hyprotech system based on HYSIM. Other programs in this package are the properties package HYPROP and the dynamic simulator HYSYS.

29.9.7 CADCentre system
The CADCentre suite centres on PEGS and PDMS, described below, linked by Design Manager.

29.9.8 ICI system
Another illustration of the facilities available in a CAPE system is the suite of programs developed by ICI. These include: PROVUE 2D, for two-dimensional graphics; PROVUE 3D, for three-dimensional graphics; TABLES and PHYSPAK, for physical properties; FLOPACK, for flowsheeting; PIPER for fluid flow; and DISTPACK and RADFRAC for distillation.

This system is complemented for manufacturing processes by PROPHET, which covers manning, working practices, production scheduling, de-bottlenecking and buffer storage sizing. For pipework it is complemented by ISOGEN for piping isometrics, ISOSTEEL for structural steelwork, and CAMS and MCPS for photogrammetry.

29.9.9 Davy system
A flowsheet simulator oriented to environmental aspects is the ESP system of Davy Energy and Environment. This is described in Section 29.29.

29.10 Plant Layout

Programs for plant layout also play an important role in the CAD of process plants. A plant layout program is another type of program which may be used as the basis of integration.

The plant layout programs considered here are three-dimensional programs oriented specifically to the layout of process plants. They include:

AutoPLANT Designer (ADA)
CADPIPE STRUCTURAL (ISS)
Design Review (Intergraph)
Dimension III (Computervision)
OMNI-EQUIP (Applications Development)
PDMS (CADCentre)
PDS (Intergraph)
PRO-PLANT/STEEL (Applications Development)
PROVUE 3D (ICI)

There are also programs which allow the designer to 'walk through' the plant. These include:

CADPIPE WALKTHRU (ISS)
REVIEW (CADCentre)

Some programs which deal with specialized aspects of plant layout are:

AutoPLANT Cable Scheduler (EDA) Cable routing
EXTRAN (NRC) Control room air intake quality

EXTRAN is described by the Nuclear Regulatory Commission (NRC) (1991 NUREG/CR-5656).

A plant layout program can provide the basis for a number of computer aids for dealing with hazards and it is therefore appropriate to consider such a program in rather more detail. The program considered is PDMS.

29.10.1 PDMS: background
The Piping Design Management System (PDMS) was developed at the CADCentre in Cambridge with the co-operation of two industrial organizations, Isopipe Ltd and Akzo Engineering BV. It was first released in 1977. It is described in *Computer-Aided Process Plant Design* (Leesley, 1982). PDMS is a major package. The 1982 version represented some 70 person-years work.

29.10.2 PDMS: project functions
PDMS has the capability to perform the following project functions:

(1) analysis of layout designs –
  (a) conceptual designs,
  (b) detailed designs;
(2) checking of designs against standards;
(3) control of project information;
(4) generation of documents and listings;
(5) archiving of project information.

29.10.3 PDMS: system structure
PDMS is structured as a group of data bases. Information is passed between these data bases by means of an information highway. The package includes the following data bases:

(1) design data;
(2) component catalogue;
(3) pipe specifications;
(4) steelwork specifications;
(5) drawing registry;
(6) project control data.

29.10.4 PDMS: program modules
The PDMS package is in modular form. The structure of the modules is shown in Figure 29.1, which also gives their names.

The module ADMIN is the project co-ordinator's administration module, and access to it is normally restricted to him. It allows him to control the databases, the access by users and the approval of designs. MONITOR mediates the user's access to databases and applications programs. RECONFIGURER performs housekeeping on the databases.

There are two modules for the two-dimensional graphics. DRAGON is the general purpose two-dimensional graphics module. The drawing constructor DRAWCON generates engineering drawings. DRAGON is used to generate piping and instrument diagrams. A DRAGON diagram can be interrogated to obtain the associated data such as equipment lists, materials schedules, etc.

CATCON handles the component catalogue. SPECON handles the specifications.

The design constructor DESCON is the main module for creation of the layout. It contains the basic three-dimensional model of the plant. The interactive equipment constructor INTERCON is used to manipulate the location of equipment. The steel erection constructor ERECON is used to create steel structures.

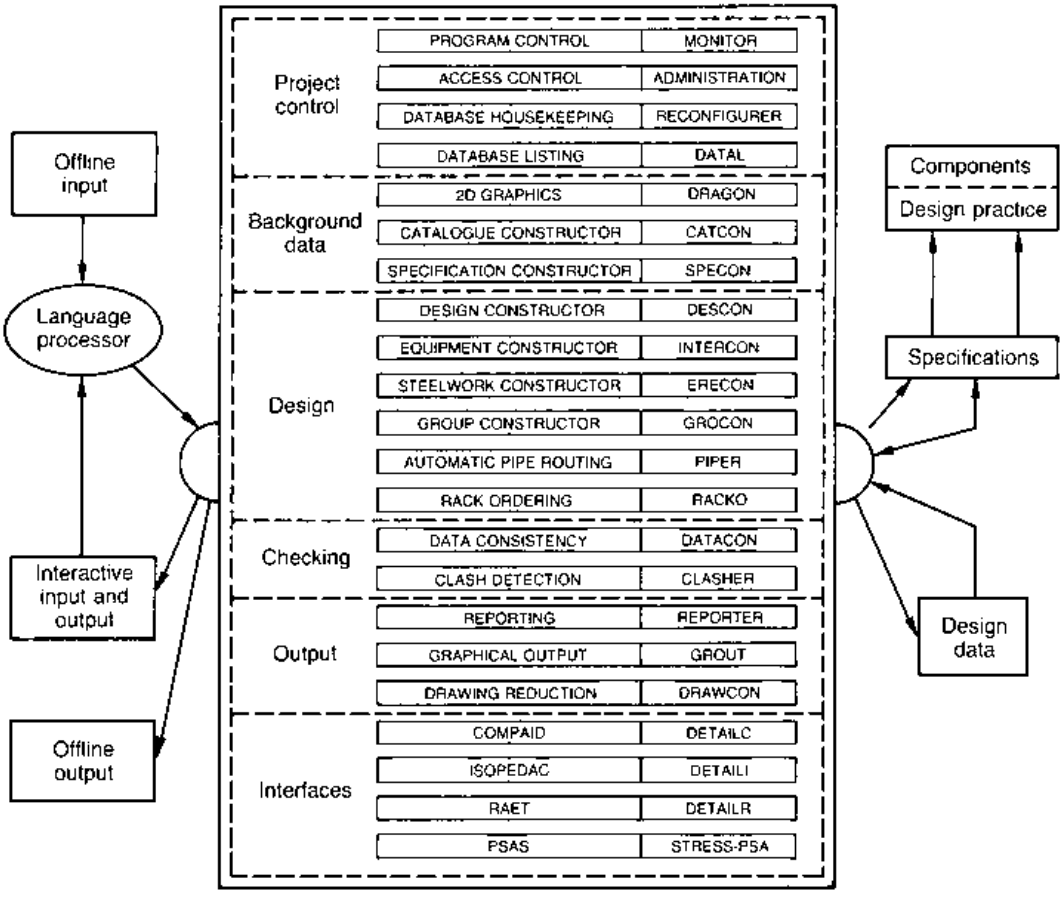


Figure 29.1 *Structure of PDMS (Leesley, 1982) (Reproduced by permission of Gulf Publishing Company)*

The group constructor GROCON allows elements to be grouped for the purposes of drawing, reporting, etc.

Piping is handled by several modules. The automatic pipe router PIPER generates a centre line for pipework between specified points. The detailed design of the pipework is then carried out through DESCON. The rack orderer RACKO is used to route pipes along racks.

The design consistency checker DATACON performs consistency checks on the pipework and adjoining equipment. The clash detection module CLASHER checks for interference or clashes between components in space.

The database lister DATAL provides outputs of the databases. The drawing constructor DRAWCON generates drawings, the graphical output module GROUT generates graphical output and the schedule production module REPORTER generates reports and schedules.

29.10.5 PDMS: design process

The starting point for the design of a plant layout using PDMS is normally the piping and instrument diagram. The PI data are held in DRAGON. The two-dimensional piping and instrument diagram is then used to create a three-dimensional layout by locating in turn the principal items of equipment, the supporting structure and the piping. The equipment items are located in three-dimensional space. The supporting steelwork is added. The piping centre lines are obtained and the pipework components entered.

Checks are carried out to ensure that there are no interferences between components and that specifications have not been violated. Documentation may then be obtained in the form of drawings and reports. Some of the graphical outputs available are illustrated in Figures 29.2 and *29.3*. Report outputs may also be obtained.

29.10.6 PDMS: hazards related enhancements

Work is currently being done to enhance PDMS by the provision of facilities for hazard assessment and for handling other hazards-related aspects such as hazardous area classification.

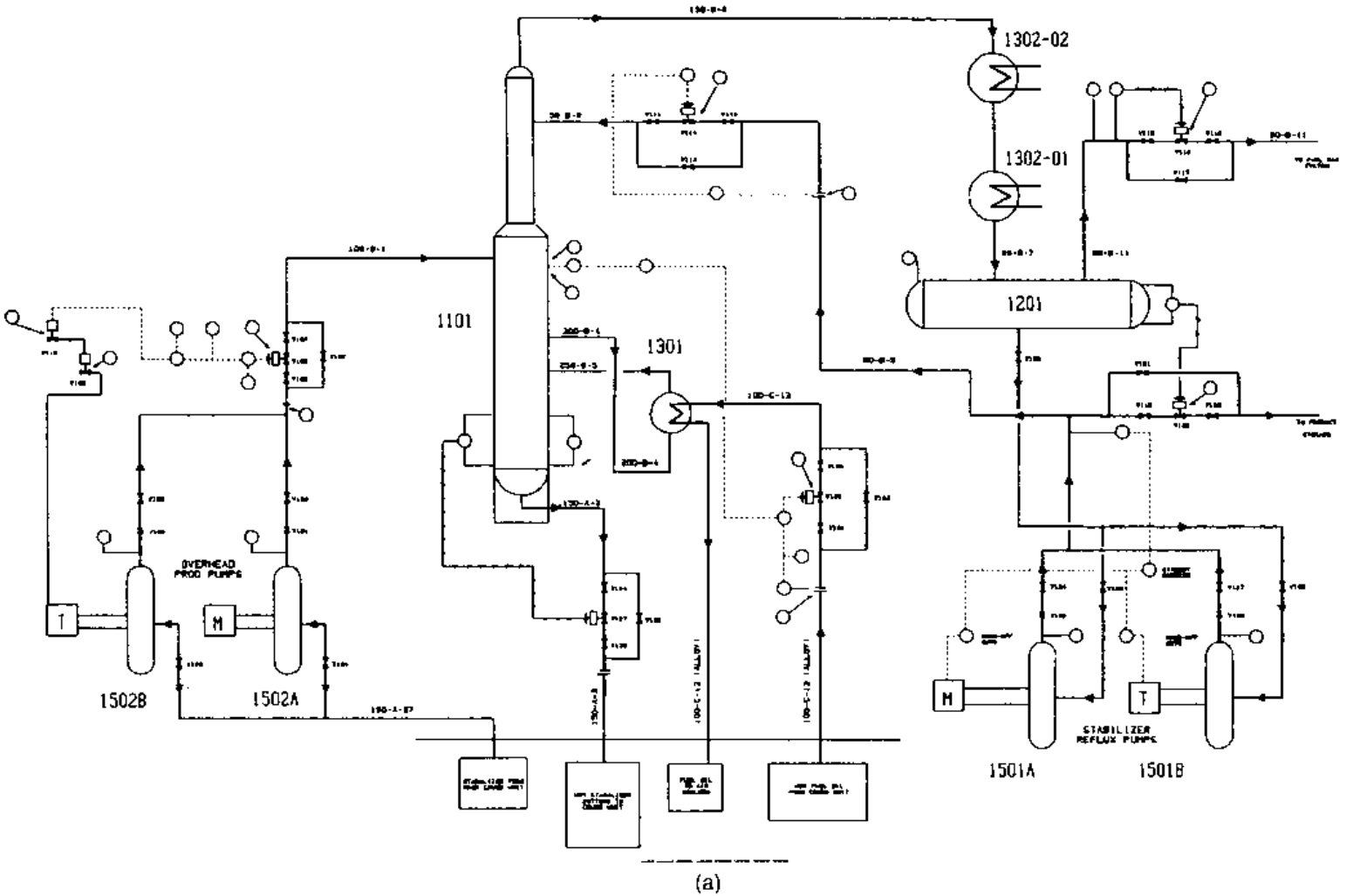
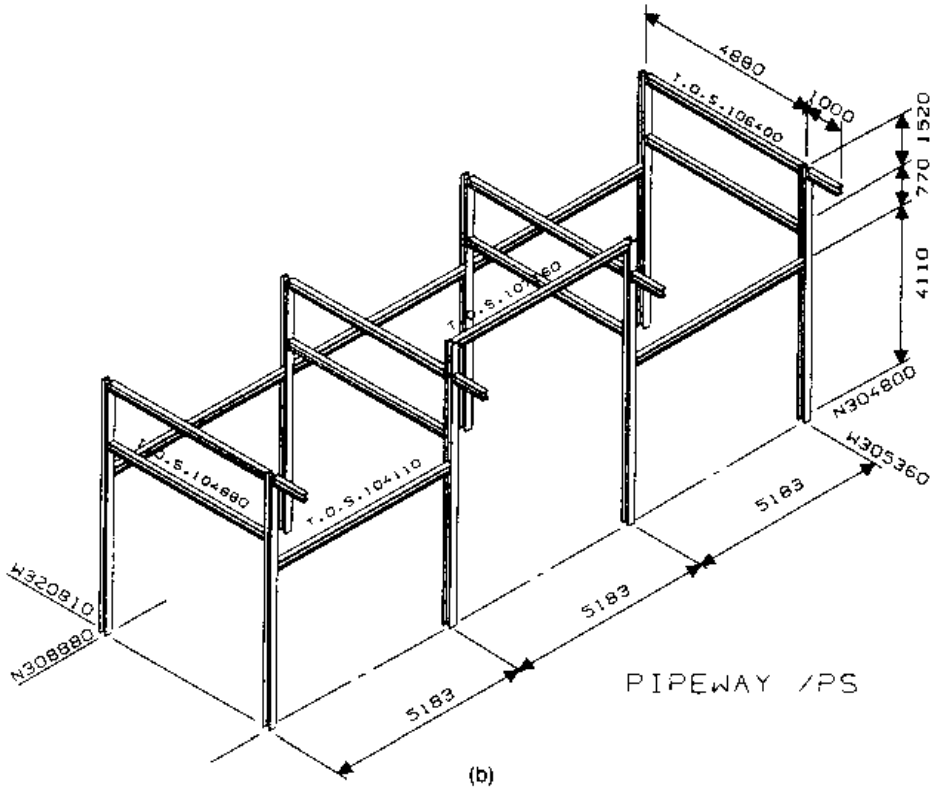


Figure 29.2 *Graphical outputs from PDMS (Leesley, 1982): (a) equipment specification; (b) steelwork; (c) pipework; (d) check on pipework details; (e) check for interference; (f) drawing; (g) detail enlargement (Reproduced by permission of Gulf Publishing Company)*



(b)

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P D.M.S. CONSTRUCTION LANGUAGE
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                PIPE /250-B-5
                -------------

NEW PIPE /250-B-5
SPEC /A3B

NEW BRAN /250-B-5/1
CONN PH TO /1301-S2
CONN PT TO /1101-N2

NEW GASK SEL
CONN TO PH
NEW FLAN SEL WITH STYP WN
CONN

NEW ELBO SEL
THRO PT
DIR E

NEW RED
FLIP
SEL WITH LBOR 250
CONN

NEW TEE SEL
THRD PT
ARR1 LEAV3
OR1 AXP PJ IS E

PREV
CONN TO NEXT
NEXT

NEW FLAN SEL WITH STYP WN
NEW GASK SEL
CONN TO PT
PREV
CONN TO NEXT

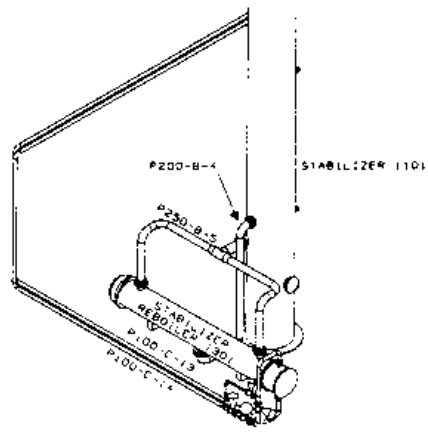
NEW BRAN /250-B-5/2
CONN PH TO /1301-S3
CONN PT TO TEEL OF BRANCH1

NEW GASK SEL
CONN TO PH
NEW FLAN SEL WITH STYP WN
CONN

NEW ELBO SEL
THRD PT
DIR E

NEW ELBO SEL
DIST 1000
DIR S

NEW RED
FLIP
SEL WITH LBOR 250
CONN TO PT
```



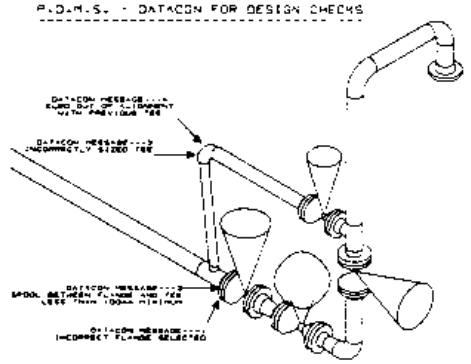
(c)

P.D.M.S.-DATACON

CHECKS ON CONSISTENCY, INTEGRITY, GEOMETRY.

DATACON LISTING DATE 09 APR 80 TIME 16.05
PIPE /100-C-12
BRAN /100-C-12/1
FLAN 5 =56/807
D410 BAD ARRIVE GEOMETRY ——————1
TEE 2 /100-C-12/1-T2
D400 ARRIVE TUBE LESS THAN TUBE MINIMUM ——2
BRAN /100-C-12/2
ELBO 1 =57/802
D420 BAD ARRIVE BORE ——————3
D410 BAD ARRIVE GEOMETRY ——————4

P.D.M.S. - DATACON FOR DESIGN CHECKS



(d)

P.D.M.S. - CLASHER - DETECTS INTERFERENCE

DATE 30 APR 79 TIME 16.42

CHECK FOR CLASHES BETWEEN

BRAN /80-A-11/2 TUBE BETWEEN TEE 1 /80-A-11/2-T2 AND ELBO 1 =19/401
STRU /PS-D3 BOX 2 =10/4705
AT SITE COORDS W310715 N300505 U105665
*** HARD/HARD CLASH ***

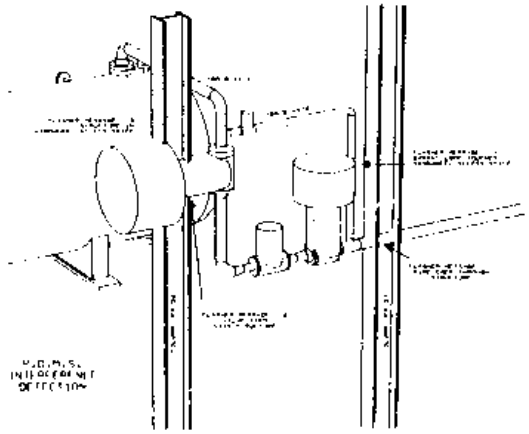
BRAN /80-A-11/2 TUBE BETWEEN TEE 1 /80-A-11/2-T2 AND ELBO 1 =19/401
STRU /PS-D3 BOX 3 =10/4706
AT SITE COORDS W310715 N300285 U105665
*** HARD/HARD CLASH ***

BRAN /80-B-14/1 VALV 1 =16/4308
STRU /PS-D2 BOX 1 =10/4707
AT SITE COORDS W310740 N298406 U106557
*** HARD/HARD CLASH ***

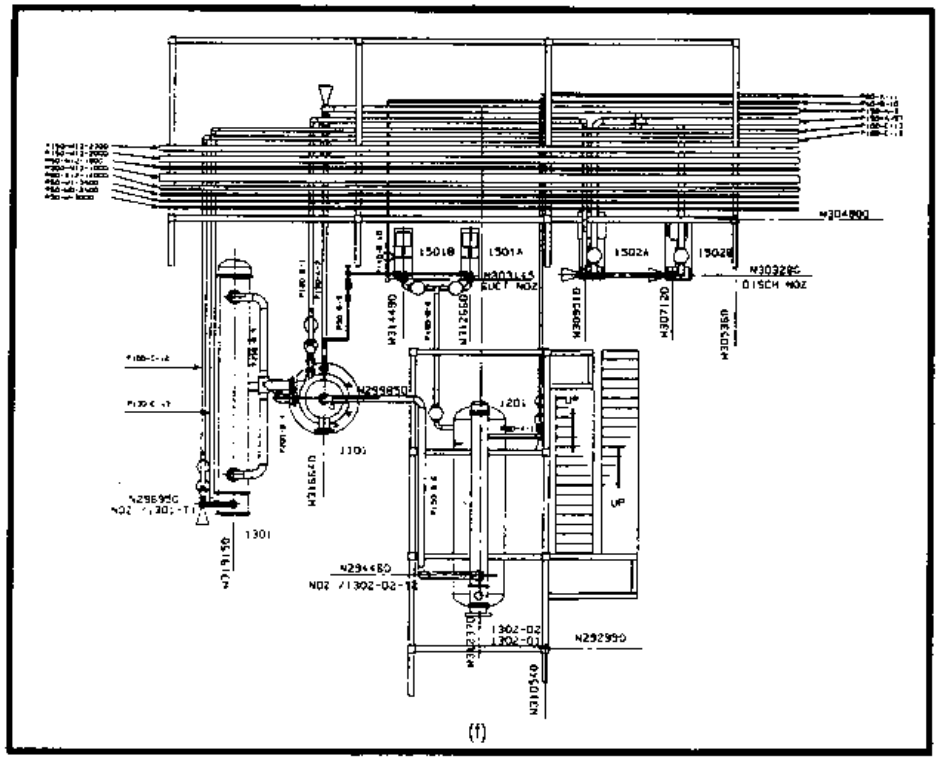
BRAN /80-B-14/1 VALV 1 =16/4308
STRU /PS-D2 BOX 2 =10/4708
AT SITE COORDS W310740 N298505 U106557
*** HARD/HARD CLASH ***

BRAN /80-B-14/1 VALV 1 =16/4308
STRU /PS-D2 BOX 3 =10/4705
AT SITE COORDS W310740 N298285 U106557
*** HARD/SOFT CLASH ***

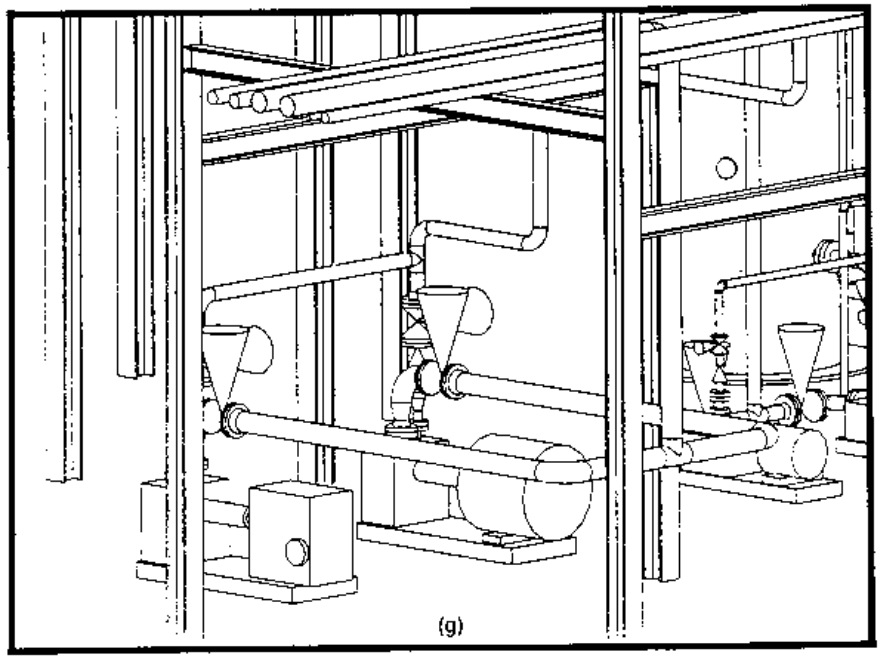
BRAN /80-B-14/2 TUBE BETWEEN ELBO 1 =17/4305 AND TAIL
BRAN /80-B-11/2 VALV 1 =15/4008
AT SITE COORDS W310715 N300050 U106294
*** HARD/SOFT CLASH ***



(e)


N304800
1501B
1501A
1502A
1502B
N303280
DISCH NOZ
N303145
DUCT NOZ
N314490
N312660
N309510
N307120
N305360
N299850
1201
1101
N316640
N296950
1301
N319150
N294480
N292990
1302-02
1302-01
N310540
UP

(f)



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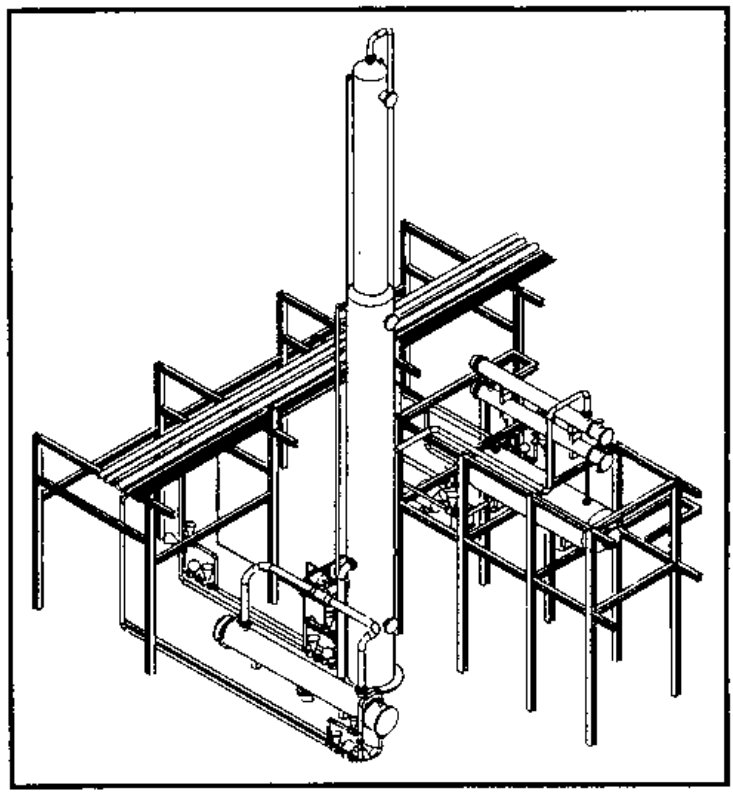

Figure 29.3 *Graphical outputs from PDMS (Leesley, 1982): isometric of the complete plant (Reproduced by permission of Gulf Publishing Company)*

29.11 Process Dynamics and Control

29.11.1 Dynamic simulation

There are several dynamic simulation packages. Early packages of this type were:

CSMP (IBM)
DSL/77

Among the packages developed specifically for the process industries are:

DPS (CADCentre)
DSNP (Dynamic Simulator for Nuclear Power Plants) (System Simulation and Analysis)
DYFLO (Franks)
DYNSYS (Domtar)
Plant Manager (PPS Systems)
SPEEDUP (Aspen Technology)

The dynamic simulation of process plants is discussed in *Mathematical Modeling in Chemical Engineering* (Franks, 1967).

Also relevant are general equation solvers such as:

PM Solver (Digital Analytics)
Simusolv (Dow Chemical Co.)

29.11.2 Control system design

Packages are also available for control system design. They include:

INDECS (CADCentre)
SPEEDUP (Aspen Technology)

29.11.3 SPEEDUP

SPEEDUP is a process design, dynamic simulation and plant optimization program. It may be used as a process simulator and has already been mentioned as such, but its strength lies in dynamic simulation.

The facility includes: a generalized physical properties interface GPPI, which may be linked to physical and thermodynamic property databases; links to other databases; a library of models; a model configuration program; and an external data interface to link to control systems for on-line monitoring, optimization and operator training.

Accounts of SPEEDUP and its development have been given by Sargent and Westerberg (1964), Sargent, Perkins and Thomas (1982) and Pantiledes (1988).

29.11.4 Instrument system design

Programs for the design of instrument systems include:

AutoPLANT Instrumentation Index (EDA)
AutoPLANT Loop (EDA)
INSTRUCALC (Dynacomp)
Instrument Configurator (Fischer and Porter)

29.11.5 Real-time systems

Examples of real-time packages are:

Table 29.3 *Some computer-based data bases*

A Physical, chemical and toxic properties

Code	*Organization*[a]
CHEM-BANK	Silver Platter
RTECS	
HSDB	
CHRIS	
OHMTADS	
OSH-ROM	
NIOSHTIC	
HSELINE	
CISDOC	
TOXLINE PLUS	
TOXLINE	
RISKLINE	
PEST-BANK	
EINECS	
INIS	
MEDLINE	
CANCER	
Bretherick Reactive Chemical Hazards Database	Butterworth-Heinemann
CHEMSAFE	STN Int.
CHEMTOX	Resource Consultants
CB	ILO
EMBASE	Elsevier Science Publs
IDLH	Government of Ontario
IRIS	CIS
PC CHRIS 93	Hazmat America

B Thermodynamic, vapour–liquid equilibrium and mixture properties

Code	*Organization*[a]
CHEMCO	CESS
JANAF	STN Int.
NIST Thermophysical Properties of Pure Fluids	NIST
NIST Thermophysical Properties of Refrigerant Mixtures	NIST
NIST Mixture Property Database	NIST
NIST THERMO	NIST
REFRIG	Technical Database Services
THERM	CIS
Thermosim Equil	Gulf
TRC Data Bases for Chemistry and Engng Vapor-Liquid Equilibria in Binary Systems	TRC
TRCTHERMO	STN Int.
VLE	AIChE
VLESET	CESS

C Incidents

Code	*Organization*[a]
MHIDAS	SRD
EIDAS	
EnvIDAS	
FACTS	TNO
HARIS	RM Consultants

[a] For acronyms of the names of organizations, see Section 29.2.

Batch Process Advisor (Stone and Webster)
CAMILE (Dow Chemical Co.)
Chemflex Batch Automation Software (Fischer and Porter)

29.12 Databases, Bibliographies and Indexes

29.12.1 Physical, chemical and toxic properties

There are a number of databases, or data banks, for the physical, chemical and toxic properties of materials. The databases are often associated with an official body.

The physical and thermodynamic property packages which support basic process design systems have been described in Section 29.4. Some other databases on physical, chemical and toxic properties that are available on computer are listed in Table 29.3, Section A.

The systems operated by Silver Platter include the following. CHEM-BANK contains: (a) RTECS (Registry of Toxic Effects of Chemical Substances), supplied by the National Institute for Occupational Safety and Health (NIOSH); (b) HSDE created by the NLM as part of its Toxnet data system; (c) OHMTADS (Oil and Hazardous Materials Technical Assistance Data System), supplied by the Environmental Protection Agency (EPA); and (d) CHRIS (Chemical Hazard Response Information System), supplied by the US Coast Guard. OSH-ROM contains: (a) NIOSHTIC, supplied by the NIOSH; (b) HSELINE, supplied by the Health and Safety Executive (HSE); (c) CISDOC, supplied by the International Occupational Safety and Health Information Centre of the International Labour Office (ILO); and (d) MHIDAS, covering hazardous incidents, supplied by the Safety and Reliability Directorate (SRD). TOSLINE PLUS contains: (a) TOXLINE, supplied by NLM; (b) RISKLINE, supplied by the National Chemical Inspectorate of Sweden; and (c) several other private sector data bases, including BIOSIS, CAS, IPA and TOXBIB. PEST-BANK, supplied by the National Pesticide Information System, gives the key registration data of all US registered pesticides.

EINECS (European Inventory of Existing Commercial Chemical Substances) is an inventory of European commercial chemicals. INIS (International Nuclear Information System) is supplied by the IAEA. Medical databases include MEDLINE and CANCER.

Another set of databases are those from Microinfo. They include HAZARDTEXT (safe handling and incident response), INFOTEXT (regulatory listings), MEDITEXT (evaluation of exposed individuals) and SARATEXT (toxicity, Sara Title III) as well as CHRIS, HDSB, IRIS, OHM/TADS and RTECS.

The Bretherick Reactive Chemical Hazards Database is the database version of the *Handbook of Reactive Chemical Hazards* (Bretherick, 1990b).

CHEMSAFE and CHEMTOX are, respectively, compendia of the flammability and toxic properties of a large number of substances.

A number of speciality databases on medical subjects are available from Elsevier Science Publishers, including the Excerpta Medica database EMBASE.

IRIS is a database of monographs in support of the assessment of the risk from a large number of chemicals.

PC CHRIS 93 gives the USCG CHRIS system, also available through Silver Platter, as described above.

Some programs for thermodynamic, vapour–liquid equilibrium and mixture properties are listed in Table 29.3, Section B.

29.12.2 Material safety data sheets

Programs for access to or management of material safety data sheets (MSDSs) include:

Baker (CIS)
MSDS ACCESS (Resource Consultants)
MSDS Engine (Genium Publishing)
MSDS ExPERSS (Imagetrak Software)
MSDSFILE (Hazmat Control Systems)
MSDS-Rite (Byte Rite)
TrackRite (Byte Rite)

TrackRite is a tool for tracking the MSDSs received from suppliers and sent to customers.

29.12.3 Mechanical engineering databases

Mechanical engineering databases include COMPENDEX-4 (Engineering Information) and ISMEC-10 (Cambridge Scientific Abstracts).

29.12.4 Incident databases

There are a number of computer-based data banks giving details of incidents involving hazardous materials. Some of the principal incident data banks are shown in Table 29.3, Section C.

There are three incident data banks operated by SRD. MHIDAS is the Major Hazard Incident Data Service. The other two are the Explosion Incidents Data Service (EIDAS) and the Environmental Incidents Data Service (EnvIDAS).

In addition to MHIDAS, AEA Technology offers the AIRS code for the recording of incidents in the workplace.

Another computer-based incident data bank is FACTS, of TNO.

29.12.5 Failure databases

Databases for failure and event data are discussed in Appendix 14. The main data banks are computer based. Among the principal failure databases are the SRD data bank, the COMPI database of TNO and, for offshore, the OREDA database. AEA Technology offer Data Base Manager which may be used to create reliability or incident databases.

29.13 Standards, Codes and Bibliographies

29.13.1 Standards and codes

Many organizations now provide their standards and codes on CD-ROM.

29.13.2 Bibliographies and indexes

Increasingly, bibliographies and indexes are becoming available on CD-ROM. Two such collections relevant here are:

(1) IChemE Safety and Environmental Index (IChemE) – indexes for relevant IChemE journals;
(2) Electronic Chemical Process Quantitative Risk Analysis Bibliography – bibliography for CCPS *QRA Guidelines*.

29.14 Compliance Management

There are quite a large number of programs to assist with compliance with regulatory requirements, mainly for the USA. Some examples are:

Chemical Compliance Monitor (Logical Technology) Chemicals regulated
Fast Regs (OSHA-Soft) OSHA and EPA regulations text search
HazReg (Genium Publishing) Chemicals regulated
HAZWASTE Hazardous waste
MSDS Engine (Genium Publishing) MSDSs
Oncologic (Logichem) Carcinogens
PC Compliance OSHA Right-to-Know, EPA SARA Title III
REGMAT (CIS) Regulations affecting chemicals
SARA (OSHA-Soft) SARA
Spill Release Advisor (OXKO) Spills

29.15 Combustion

Programs for combustion calculations include:

Combust (Tecs Software)
Combustion Analysis (Thermal Analysis Systems)
Gas Combustion (Techdata)

Adiabatic flame temperature can be performed using:

FLAME (Tecs Software)

29.16 Computational Fluid Dynamics

Codes for computational fluid dynamics (CFD) find widespread use both in design and in hazard assessment. Accounts are given by Sharratt (1990), C. Butcher (1991a) and Swithenbank (1991). General purpose CFD packages include:

ASTEC (CFD Services)

Table 29.4 *Some computer codes for hazard identification*

A Hazop	
Code	*Organization*
Hazard Manager	AEA Technology
HAZOP-PC	PrimaTech
HAZOPtimizer	AD Little
HAZSECplus	DnV Technica
B Other techniques	
Code	*Organization*
AUDIT-PC	PrimaTech
FMEA	JBF Associates
FMEA-PC	PrimaTech
MANAGE-PC	PrimaTech
PHA-PC	PrimaTech
WHAT-IF-PC	PrimaTech

FLOSYS
FLOW3D (CFD Services)
FLUENT (Fluent)
PHOENICS (Cham)
STAR

There are also specialist CFD programs such as:

RAD3D (CFD Services) Radiant heat transfer

A typical application of CFD might be the study of the ventilation flows in an offshore module. CFD is also the basis of codes for the simulation of explosions, the combustion reaction being added to the basic fluid dynamics.

29.17 Hazard Identification

There are available a number of codes to assist in the conduct of the various techniques for hazard identification. Some of these aids are listed in Table 29.4.

Aids for hazard and operability (hazop) analysis are given in Table 29.4, Section A. These assist particularly with the housekeeping and follow-up aspects.

29.17.1 DnV Technica suite

The program HAZSECplus of DnV Technica provides an aid for the checklist, failure modes and effects analysis, hazop and what if? methods, including facilities to track the recommendations resulting.

29.17.2 Primatech suite

The Primatech family of codes includes HAZOP-PC and other codes shown in Table 29.4, Section B. The titles are largely self-explanatory. MANAGE-PC is a program for managing the various recommendations which arise from hazard analysis studies and PHA-PC is a program for preliminary hazard analysis, or the initial screening of hazards.

Table 29.5 *Some computer codes for reliability engineering*

Code	*Subject*	*Reference/ organization*
ALMONA	Reliability analysis of logical networks	Brock (1977)
CARA	Reliability tool kit, fault trees, event trees, failure modes, effects and critical analysis	DnV Technica
PLANT	Reliability and availability analysis	C.S. Windebank (1983)
PROTECT	Trip system analysis	Kumamoto, Inoue and Henley (1981)
RELCODE	Failure data analysis	Hastings and Jardine (1979)
RELDAT	Reliability database	AEA Technology
SAFE-D, SAFE-R	Failure data analysis	NRC (1981 NUREG CR/2375)
SNAP	Sneak analysis	Sigma-Lambda Software
STAR	Reliability and availability analysis	Davidson and Macdonald (1977)
SUPERNET	Reliability and risk assessment	WS Atkins (1991)
VISA II	Pressure vessel reliability	NRC (1986) NUREG/ CR4486)

Table 29.6 *Some computer codes for fault tree drafting*

Code	*Reference/organization*
FAULTrease	AD Little
FaultTree	Isograph
ORCHARD	SRD
SCEH	Henley (1977)
SUPER-TREE	WS Atkins (1991)
TREDRA	L.S. Baker *et al.* (1978)
TREE	Brock (1977)

29.17.3 AEA Technology suite

The AEA Technology suite includes Hazard Manager for the recording and follow-up of hazop studies and Safety Audit Manager for the conduct of operational audits.

29.18 Reliability Engineering and Fault Trees

There are available a number of codes for reliability engineering calculations. Some of these codes are listed in Table 29.5.

29.18.1 Trip system design

The code PROTECT gives estimates of the quantities of interest in the design of trip systems such as the frequency of the demand and of the functional and operation failures. An account is given by Kumamoto,

Table 29.7 *Some computer codes for fault tree analysis*

A Basic analysis

	Minimum cut sets	*Common cause failures*	*Reliability/ availability*	*Reference/organization*[a]
ALLCUTS	×			van Slyke and Griffing (1975)
BACFIRE		×		Cate and Fussell (1977)
BACFIRE II		×		Rooney and Fussell (1978)
BFR		×		Attwood and Suitt (1983)
BRAVO	×	×	×	JFB Associates
CAFTA+PC	×			Science Applications Inc.
CARA	×			SINTEF, Technica
COADE	×			COADE
COMCAN		×		Burdick, Marshall and Wilson (1976)
COMCAN II		×		Rasmuson *et al.* (1978)
CUTSET	×			WS Atkins
ELRAFT	×			Semanderes (1971)
FATRAM	×			Rasmuson and Marshall (1978)
FAULTRAN	×			Wheeler *et al.* (1977)
FAUNET	×		×	Platz and Olsen (1976)
FRANDOM			×[b]	Goldberg and Vesely (1977)
FRANTIC			×[b]	Vesely and Goldberg (1977)
FRANTIC II			×[b]	NRC (1981 NUREG/CR-1924)
FTAP	×			ORNL
GO			×	Gateley, Stoddard and Williams (1968); Gately and Williams (1978)
IRRAS-PC	×			EGG
KITT			×[b]	Vesely and Narum (1970)
LOGAN	×			RM Consultants
MFAULT	×			Pelto and Purcell (1977)
MICSUP	×			Pande, Spector and Chatterjee (1975)
MOCUS	×			Fussell, Henry and Marshall (1971)
PATREC	×		×	Blin *et al.* (1977)
PL-MOD	×	×	×	Olmos and Wolf (1977)
PREP	×			Vesely and Narum (1970)
SALP-3	×	×	×	Astolfi *et al.* (1978)
SETS	×	×	×	Worrell (1974, 1985); NRC (1985, NUREG/CR-4213)
SUPERPOCUS			×	Fussell *et al.* (1977)
WAM-BAM			×	Erdmann *et al.* (1977)
WAMCOM		×		Putney (1981)
WAMCUT	×		×	Erdmann *et al.* (1977)

B Importance

Code	*Reference/organization*
IMPORTANCE	Lambert and Gilman (1977a,b); NRC (1981 NUREG/CR-1965)
PL-MOD	See above
SENS	W.S. Atkins
SUPERPOCUS	Lambert and Gilman (1977a,b)

C Quantitative analysis

Code	*Reference/organization*
CAFTA+PC	Science Applications Inc.
CARA	SINTEF, Technica
COADE	COADE
IRRAS-PC	EGG

D Uncertainty analysis	
Code	*Reference/organization*
ESCA	Laviron (1985)
FRANDOM	See above
MOCARS	AEC (1975)
PATREC	See above
SAMPLE	AEC (1975)
SPASM	Erdmann *et al.* (1978)
STADIC	Cairns and Fleming (1977)
E Overall package	
Code	*Reference/organization*
Fault Tree Manager	AEA Technology

[a] See Table 29.1 for further references.
[b] Handles time dependence.

Inoue and Henley (1981). Details have been given in Chapter 13.

29.18.2 Fault tree drafting

Aids to fault tree drafting are listed in Table 29.6.

29.18.3 Fault tree analysis

Table 29.7 gives details of aids to fault tree analysis. These cover the determination of the minimum cut sets, analysis for common cause failure (CCF), assessment of importance and sensitivity, quantitative analysis and uncertainty analysis.

BRAVO (JBF Associates) is a program for performing reliability, availability and maintainability analysis and fault tree and event tree analysis.

CARA (SINTEF, DnV Technica) provides an aid for the analysis of reliability data, failure modes effects and criticality analysis, fault tree analysis and cause–consequence analysis.

SUPERNET (WS Atkins) is a package for reliability analysis, risk assessment, and life-cycle costing. It contains the codes SUPER-TREE for fault tree handling, CUTSET for fault tree analysis, SENS for sensitivity and importance analysis, FRANTIC for time-dependent reliability analysis, SAMPLE for statistical uncertainty analysis and COST for life-cycle costing.

29.18.4 Dependent failure analysis

The computer codes used by the Safety and Reliability Directorate (SRD) for dependent failure analysis are described by Humphreys and Johnson (1987 SRD R418).

29.18.5 Failure data analysis

There are numerous mathematical packages which may be used to analyse failure and other data to obtain the distribution function, e.g. Probability Distribution Plotting (TEAM Graph Papers).

29.18.6 STARS

STARS is a suite of knowledge-based tools for safety and reliability analysis. An overview is given by Poucet (1990).

Table 29.8 *Some computer codes for event tree analysis*

Code	*Organization*	*Reference*
BRAVO	JFB Associates	
CARA	SlNTEF, Technica	
ETA II	Science Applications Inc.	
EVNTRE	NRC	NRC (1989 NUREG/CR- 5174)
METEOR	RM Consultants	
MULTIPLET	SRD	Hall (1984 SRD R300)
RISKMAN	Pickard, Lowe and Garrick Inc.	
SUPER	Westinghouse	

29.19 Escalation and Event Trees

29.19.1 Escalation

The escalation of a fire or explosion in the confined conditions of an offshore module tends to require the consideration of a large number of potential escalation paths and has stimulated the development of computer aids. Two such aids are CASSANDRA (SRD) and PLATO (Four Elements).

29.19.2 Event tree analysis

Aids to event tree analysis are listed in Table 29.8.

29.19.3 PLATO

One of these aids is PLATO, from Four Elements. This program provides an alternative approach to the use of conventional event tree methods developed for offshore applications. It utilizes pre-programmed submodels of platform components to generate potential event sequences and to identify and simulate the different event sequences which can follow from a single initiating event such as a hydrocarbon leak.

Table 29.9 *Some computer codes developed for earthquake engineering*

A National Information Service for Earthquake Engineering codes (NISEE, 1982)

Code	*Date*	*Description*
DAMAGE	1980	Assessment of damageability for existing buildings in a natural hazards environment
EAD	1970	Earthquake analysis of dams
EORIKS	1976	Evaluation of sites for earthquake risk
ERST	1981	Earthquake response of sea-based storage tanks
EXCENTANK	1975	Response of empty cylindrical ground-supported liquid storage tank to base excitation
EXDAMTANK	1978	Seismic response of a domed cylindrical liquid storage tank
FIRES-T3	1977	Fire response of structures – thermal, three-dimensional structures
FTAP	1979	Fault tree analysis
PSDGEN	1980	Stochastic seismic analysis of piping systems subjected to multiple support excitations
PSAP		
TANKFREQ	1975	Natural frequencies of cylindrical liquid storage containers

B Other codes

Code	*Organization/reference*	*Description*
CARES	NRC (1990 NUREG/CR- 5588)	Seismic evaluation of structures
FLUSH	Ravindra (1992)	Soil–structure interaction
SHAKE	Ravindra (1992)	Soil–structure interaction
HAZARD	NRC (1986 NUREG/CR- 4431)	Seismic hazard
SMACS		Soil–structure interaction

Table 29.10 *Some computer codes for emission*

A Two-phase flow

Code	*Organization*	*Reference*
BLOWDOWN	Imperial College	Haque, Richardson and Saville (1992)
BLOWSIM	UCL	
DEERS	JAYCOR Inc.	
HUBBLE-BUBBLE I, HUBBLE-BUBBLE II	SRD	Mather (1978 SRD R97), Martin (1978 SRD R118)
PIPEPHASE	Simulation Sciences Inc.	
PIPE1, PIPE2	UKAEA, Harwell	

B Emergency relief

Code	*Organization*
RELIEF	Tecs Software
SAFETY	AKC Technology
SAFIRE	DIERS

29.20 Rare Events

29.20.1 Earthquake engineering

There are a number of codes for earthquake engineering. Table 29.9 lists some of these codes.

29.21 Emission

There are a number of emission situations, particularly those involving two-phase flow, which require quite complex models and there are a number of codes. Some of these emission codes are listed in Table 29.10.

The UKAEA at Harwell have a series of codes with the generic name PIPE (e.g. PIPE1, PIPE2).

The HSE code COPTERA has been described by D.A. Carter (1986 LPB 70; 1988). This is based on the homogeneous equilibrium flow model as given in Equation 15.2.48 together with the friction factor given in Equation 15.1.64.

Table 29.11 *Some computer codes for passive gas dispersion preferred by the Environmental Protection Agency*

Code[a]	*Organization*[b]	*Reference*
BLP	ERT	Schulman and Scire (1980)
CALINE	FHA	Benson (1979)
CDM 2.0	EPA	Irwin, Chico and Catalono (1985)
RAM	EPA	D.B. Turner and Novak (1978)
ISC	EPA	EPA (1986)
MPTER	EPA	Pierce and Turner (1980)
CRSTER	EPA	EPA (1977)
UAM	SAI	Ames *et al.* (1985)
OCD	ERT	S.R. Hanna *et al.* (1984)
UNAMAP	Trinity Consultants, EPA	Finch and Serth (1990)

[a] BLP, Buoyant Line and Point Source Dispersion Model; CDM, Climatological Dispersion Model; RAM, Gaussian-Plume Multiple Air Quality Algorithm; ISC, Industrial Source Complex: MPTER, Multiple Point Gaussian Dispersion Algorithm with Terrain Adjustment; CRSTER, Single Source Model; UAM, Urban Airshed Model; OCD, Offshore and Coastal Dispersion Model.
[b] EPA, Environmental Protection Agency; ERT, Environmental Research and Technology Inc.; FHA, Federal Highway Administration.

29.21.1 Pressure relief devices

Programs for pressure relief devices sizing include:

DiscCalc (Fike) Bursting discs
INSTRUCALC (Dynacomp) General
RELIEF (Tecs Software) Fire exposure
SAFETY (AKC Technology) Fire exposure
SARVAL (ISA) Safety relief valves

29.21.2 Reactor venting

The SAFIRE code for the venting of reactors, which implements the design methods developed by the Design Institute for Emergency Relief Systems (DIERS) as part of its design package for emergency relief, has been described by Grolmes and Leung (1985). An account of this code is given in Chapter 17.

29.21.3 Blowdown

Programs which calculate the emission flows from vessels, pipes and pipelines are:

BLOWDOWN (Imperial College)
BLOWSIM (UCL)

An account of BLOWDOWN is given by Haque, Richardson and Saville (1992).

29.22 Gas Dispersion

One of the most important topics covered by such codes is gas dispersion, particularly dense gas dispersion. An account of gas dispersion models was given in Chapter 15. Different models are used for passive and dense gas dispersion.

A review of gas dispersion models with special reference to computer codes is given in *Air Pollution Modeling: Theories, Computational Methods and Available Software* (Zannetti, 1990).

29.22.1 Passive gas dispersion

Models for passive gas dispersion were described in Chapter 15. Manual calculation is possible with the simpler forms of model, but for most practical applications, particularly in air pollution modelling, use is made of computer codes.

There are now a large number of codes for specific situations such as multiple sources, complex terrain, urban conditions, and coastal and offshore locations.

Certain codes are advised by the EPA as 'preferred' codes for air pollution modelling. These are given in Table 29.11. Most of these are contained within the UNAMAP system of air quality models. The codes are listed with full details by Zannetti (1990). Zannetti also lists the codes advised by the EPA as 'alternative' as well as a large number of other programs.

29.22.2 Dense gas dispersion

Models for dense gas dispersion, also described in Chapter 15, have tended to be much more complex than those for passive dispersion, and for most such models a computer program is essential. Some of codes for dense gas dispersion are listed in Table 29.12.

One of the most comprehensive and up-to-date codes is DRIFT (AEA Technology).

29.22.3 BREEZE suite

In addition to the codes listed in the tables, Trinity Consultants offer the BREEZE suite:

BREEZE Air Complex-1	Air pollution, complex terrain
BREEZE AIR ISCLT2	Air pollution, long-term
BREEZE AIR ISCST2	Air pollution, short-term
BREEZE AIR SCREEN	Air pollution, screening
BREEZE HAZ	Hazard assessment model selection
BREEZE HAZ DEGADIS	Hazard assessment, DEGADIS model
BREEZE HAZ INPUFF	Hazard assessment, INPUFF model
BREEZE HAZ SPILLS	Hazard assessment, evaporation
BREEZE HAZ WAKE	Hazard assessment, building wakes

Table 29.12 *Some computer codes for dense gas dispersion*

A Major codes

Code	*Organization*	*Reference*
AIRTOX		Paine *et al.* (1986)
CARE		Verholek (1986)
CHARM	Radian Corp.	Balentine and Elgroth (1985); Radian Corp. (1986); NRC (1988 NUREG/CR-5162)
CHLORINE	Chlorine Institute	
CIGALE 2	Centre d'Etudes Nucléaires	Cabrol, Roux and Lhomme (1987)
COBRA III	Concord Scientific Corp., Environment Canada	Oliverio *et al.* (1986)
CRUNCH	SRD	Jagger (1983 SRD R229)
DEGADIS	University of Arkansas, USCG	Havens and Spicer (1985)
DENS20		Meroney (1984a)
DENZ	SRD	Fryer and Kaiser (1979 SRD R152)
DISP2	ICI	Fielding, Preston and Sinclair (1986)
DISCO	SIA	Gratt and McGrath (1975b)
DRIFT	SRD	Mercer and Porter (1991); Byrne *et al.* (1992 SRD R553); Webber *et al.* (1992 SRD R586 and R587)
EAHAP	Energy Analysts Inc.	
FEM3	LLNL	Chan (1983)
GASTAR	Cambridge Environmental Research Consultants	Mercer and Porter (1991)
HASTE	Environmental Research and Technology	
HAZARD		Drivas, Sabnis and Teuscher (1983)
HEAVYGAS	WS Atkins	Deaves (1985)
HEAVYPUFF	Riso National Laboratory	Jensen (1983)
HEGAD	SWRI, API	T.B. Morrow (1982b)
HEGADAS	Shell	Colenbrander and Puttock (1983)
HEGADAS II	Shell	Colenbrander (1980)
MARIAH		Taft (1981)
MERCURE-GL	EDF	Riou and Saab (1986); Riou (1987)
MIDAS	Pickard, Lowe and Garrick Inc.	CEP (1994)
NILU		Eidsvick (1980, 1981a)
PLUMEPATH	Shell	
SAFEMODS	Technology and Management Systems Inc.	Raj (1981)
SIGMET		England *et al.* (1978)
SIGMET-N	Science Applications Inc.	Su and Patniak (1981)
SLAB	LLNL	Morgan, Morris and Ermak (1983)
SLUMPING	Royal Netherlands Meteorological Institute	
TRACE	Dupont Safer Emergency Systems	
TRANSLOC	Battelle Institute	Schnatz and Flothmann (1980)
VAPID	Riso National Laboratory	Jensen (1983)
ZEPHYR	Energy Resources Co., Exxon Research and Engineering Co.	McBride (1981)

B Other codes

Britter (1979, 1980)
van Buijtenen (1980); Verhagen and van Buijtenen (1986)
R.A. Cox and Carpenter (1980)
R.A. Cox and Roe (1977)
Fay (1980)
Fay and Zemba (1986)
Flothman and Nikodem (1980)
Germeles and Drake (1975)
Picknett (1981)
van Ulden (1988)

C Dispersion with special features

Code	*Feature*	*Reference*
FENCE62	Fence	Meroney (1991)
SPRAY65	Water spray barrier	Meroney (1991)

D Some hazard model, hazard assessment or emergency response systems containing codes

RISKAT
SAFETI
WHAZAN
CHARM
CHIEF
DISCOVER
SAFER

29.22.4 HGSYSTEM

Shell has developed for dense gas dispersion the HGSYSTEM suite of models. This suite is built around HEGADAS, the model for dense gas dispersion at ground level. Several of the other programs in the initial suite bear the prefix HF, reflecting their origins as a tool for handling the release of hydrogen fluoride. Programs in the suite include: EVAP, for evaporation from a pool; HFSPILL, for a time-varying pressurized release of gas, subcooled liquid or flashing liquid; and HFPLUME, for a pressurized release from an elevated source. Further details are given in Chapter 15.

29.23 Hazard Models

Computer codes exist for a number of hazard models, and indeed for the more complex models this is the only practical method of use. A selection of codes for a variety of phenomena is shown in Table 29.13, Section A. Some of the principal subjects are as follows: jets; vaporization from pools; pool fires; fire engulfment; flame impingement; explosion in, and explosion relief of, large enclosures; vapour cloud explosions.

Other codes for hazard models are incorporated in the hazard assessment codes described in the next section.

29.23.1 Jets

The computer code TECJET of Technica models jets of different density or buoyancy, jets with high and low velocity, jets with vertical, horizontal or angled orientation, jets in ambient wind and turbulent conditions, jets with two-phase flashing behaviour, and jets with airborne aerosol effects. Another jet program is SRD's TRAUMA (Wheatley 1987, SRD R393).

29.23.2 Vaporization from pools

Several computer codes for vaporization from pools have been developed by the SRD. These include SPILL (Prince, 1981 SRD R210) and GASP (Webber, 1990 SRD R 507). Another code for vaporization is SPILLS (Fleischer, 1980).

29.23.3 Fire events

A Technica program for the calculation of the thermal radiation from a jet flame, a pool fire or a boiling liquid expanding vapour explosion (BLEVE) has been described by J. Cook, Bahrami and Whitehouse (1990).

AEA Technology codes include PFIRE for thermal radiation from pool fires and TORCH for jet flames.

Another program for jet fires is JETFIAN (UCL).

Computer codes for the modelling of the fire engulfment of vessels include the SRD programs ENGULF (Ramskill and Hunt 1987 SRD R354) and ENGULF II (Ramskill 1989 SRD R480). Other fire engulfment programs are VT*VESSEL of DnV and VRJTankheat (Meiers and Jarman, 1992).

29.23.4 Condensed phase explosions

There are a number of programs which have been developed by the military to determine the effects of explosions, nuclear explosions and condensed phase explosions, including weapons.

One of the best known codes is FRAGHAZ for determining the characteristics of the fragments from the explosion of a stack of weapons, which is described by McCleskey (1988b).

The program EXMOD, developed by Gilbert and coworkers (Gilbert, Lees and Scilly, 1994a–i) models the effects of the explosion of a condensed phase explosive, cased or uncased, in a built-up area, such as might occur in the transport of explosives. It incorporates the program EXFRAG for the effects of the fragments.

29.23.5 Vapour cloud explosions

There are several computer codes for, or applicable to, the estimation of the blast from vapour cloud explosions. W.E. Baker *et al.* (1983) describe the use of the program CLOUD for vapour cloud explosions. A code BLAST, for the simulation of the blast from a vapour cloud explosion, has been developed by TNO, as described by van den Berg (1980).

The SRD gas explosion codes are GASEX1 (Mackenzie and Martin, 1983 SRD R251) and GASEX2 (Martin, 1983 SRD R173). A more recent code is EXPEL (AEA Technology).

Table 29.13 *Some computer codes for hazard models and hazard model systems*

A Individual hazard models

Code	*Subject*	*Reference/organization*
AEROSOL	Aerosols	NRC (1981 NUREG/CR- 1367)
BLAST	Vapour cloud explosion	van den Berg (1980)
CLEAR	Evacuation	NRC (1982 NUREG/CR- 2504)
CLICHE	Explosion in large enclosure	Catlin (1990)
CLOUD	Vapour cloud explosion	W.E. Baker *et al.* (1983)
ENGULF	Fire engulfed vessel	Ramskill and Hunt (1987 SRD R354), Ramskill (1987 SRD R413)
ENGULF II	Fire engulfed vessel	Ramskill (1989 SRD R480); Ramskill and Marriott (1989 SRD R481)
EXPOSURE-I	Exposure to toxic gas cloud	D.J. Wilson (1990); D.J. Wilson and Zelt (1990); Zelt and Wilson (1990)
EVAS	Evacuation	Hesel and Schnadt (1982)
FIRE2	Pool fire in bunded area	M.J. Pritchard and Binding (1992)
FIREPLY	Pool fire	D.A. Carter (1989)
FIRENET	Fire risk assessment in buildings	Hall and Scattergood (1984 SRD R299)
FLACS	Explosion in large enclosure	Bakke, Bjerketvedt and Bjorkhaug (1990)
FLARE	Combustion – two dimensions	Martin (1986 SRD R373)
GASEX1	Gas cloud explosion – one dimension	Mackenzie and Martin (1983 SRD R251)
GASEX2	Gas cloud explosion – two dimensions	Martin (1983 SRD R173)
GASP	Vaporization from liquid pools	Webber (1990 SRD R 507)
REAGAS	Explosion in large enclosure	van den Berg (1989)
SHELTER	Shelter from toxic gas cloud	D.J. Wilson (1990); D.J. Wilson and Zelt (1990); Zelt and Wilson (1990)
SMOKE	Fire inside building	D.A. Carter (1989)
SPILL	Vaporization of liquid spills	Prince (1981 SRD R210)
SPILLS	Vaporization from liquid pools	Fleischer (1980)
TANKCAR	Jet flame impingment on rail tank car or road tanker	Birk (1989)
TECJET	Jets	DnV Technica
TRAUMA	Two-phase ammonia release	Wheatley (1987 SRD R393)
VENTEX	Explosion relief of large enclosure	Shell
VT*VESSEL	Fire engulfed vessel	DnV

B Hazard model systems

Code	*Comment*	*Reference/organization*
CHEMS-PLUS	For emergency planning	AD Little
CHAOS	For offshore platforms	British Gas
EFFECTS	Based on the *Yellow Book*	TNO
LEKCON		Technica Inc.
PHAST		DnV Technica

Another program for vapour cloud explosions is CMBWAT (Madsen and Wagner, 1994).

29.23.6 Explosions in large enclosures

Codes for the simulation of explosions in large enclosures play an important role in the design of fire and explosion protection of offshore platforms. Two such codes are FLACS and CLICHE.

The FLACS code of the Christian Michelsen Institute (CMI) solves the fundamental equations of fluid flow taking into account turbulence and combustion. The three-dimensional Navier–Stokes equations, suitably augmented to include the effects of turbulence and combustion, are cast in discrete form, employing a finite volume technique, and are solved implicitly. Turbulence is modelled in terms of eddy viscosity, and combustion is modelled in terms of a turbulent, mixing-limited reaction. The space modelled is divided into a grid of 'boxes' of $1\,m^3$ volume. Normal assumptions are that the gas cloud is a stoichiometric homogeneous, quiescent mixture. Ignition is modelled by assuming that at time zero half the flammable mixture in one of the boxes has undergone combustion. Details of the structure of the enclosure and of the equipment contained in it are captured by a front-end code CASD. Outputs of the code are the profiles of the unburnt fuel, the combustion products, the pressure, the temperature and the velocity vectors as a function of time. Some typical results are shown in Plates 27 and 28. FLACS is described by Hjertager (1982) and Bakke, Bjerkevedt and Bjorkhaug (1989).

Table 29.14 *Some computer codes for hazard assessment systems*

Code	*Organization*	*Reference*
ARCHIE	FEMA	Early, Livingston and Newsom (1990)
CIRRUS	BP	
RISKAT	HSE	Pape and Nussey (1985); Crossthwaite, Fitzpatrick and Hurst (1988); Hurst, Nussey and Pape (1989); Nussey, Pantony and Smallwood (1992)
SAFETI	DnV Technica	Ale and Whitehouse (1986); Pitblado and Nalpanis (1989)
SUPERCHEMS	AD Little	
TRANSPIRE	British Gas	Hopkins (1993); Hopkins, Lewis and Ramage (1993)
WHAZAN	DnV Technica	Technica (1986); Pitblado and Nalpanis (1989)

The CLICHE code of British Gas, described by Catlin (1990), is based on a spherical flame front. It was originally intended for use in simulating explosions in vessels with a high degree of confinement and low flame speeds, but has since been extended to make it applicable to enclosures such as modules.

Another code for explosions in large enclosures is the REAGAS code of TNO described by van den Berg (1989) and van den Berg, van Wingerden and The (1991).

29.24 Hazard Model Systems

Some hazard model systems are given in Table 29.12, Section B. These are now briefly described except for CHAOS, which is considered in Section 29.30.

29.24.1 ARCHIE

The ARCHIE code of the Federal Emergency Management Agency (FEMA), from Hazmat America, contains a set of models for a variety of scenarios cast in a tree structure, which at the first level down include pressurized gas release, liquid release followed by vaporization from the pool, a closed tank engulfed in fire, and a condensed phase eplosion, and at lower levels extend to events such as jet flame, flash fire, vapour cloud explosion and BLEVE. It is described in the *Handbook of Chemical Hazard Analysis Procedures* (FEMA, 1989) and by Early, Livingston and Newsom (1990).

29.24.2 CHEMS-PLUS

CHEMS-PLUS by A.D. Little is a simplified hazard assessment code intended for emergency planning.

29.24.3 CIRRUS

The BP hazard model system is entitled CIRRUS. It is divided into four suites of programs. The dispersion model suite contains models for: (1) the source term, based on Fauske's models, and handling aerosol and rainout; (2) jets, using the HGSYSTEM model (Witlox *et al*., 1990); (3) a link between the jet model and the gas dispersion model, using the HGSYSTEM model; (4) dense gas dispersion, using HEGADAS; (5) passive gas dispersion, using the HGSYSTEM model (Witlox *et al*., 1990); (6) passive gas dispersion, using the EPA long-term averaging model ISCLT (EPA, 1986); (7) passive gas dispersion, using the EPA short-term averaging model ISCST (EPA, 1986); and (8) particulate dispersion, based on the Sutton model (Slade, 1968).

The fire model suite has models for: (1) a pool fire, based on the model of Mudan (1984c); (2a) a gas jet flame, based on the model of Chamberlain (1987); (2b) a liquid jet flame, based on the model of Tam and Cowley (1989); and (3) a fireball, based on the model of A.F. Roberts (1981/82). The explosion model suite contains models for: (1) a vapour cloud explosion, based on the TNO multi-energy model (van den Berg, 1985); (2) a pressure burst, based on the model of Scilly and Crowther (1992); and (3) missiles from a BLEVE, based on the model of Scilly and Crowther (1992). The last suite, for source term models, contains a model for vaporization from a pool, the GASP code, based on the model of Webber (1988 SRD R404).

29.24.4 EFFECTS

The hazard models given in the TNO *Yellow Book* are available as the code EFFECTS. They include models of emission, turbulent free jets, vaporization from pools, passive gas dispersion, heat radiation and vapour cloud explosions.

29.24.5 LEKCON

LEKCON by Technica Inc. (J.L. Woodward, 1990) is a hazard model system which contains the following codes: DIPPR for physical properties; LEAKER for emission rates from vessels; LPOOL for pool spread and vaporization; JETLEK for dispersion from elevated, high momentum releases; and DEGADIS for the ground level dispersion of an aerosol or dense gas.

LEAKER extends the LEAKR model of Environment Canada by Belore and Buist (1986), LPOOL extends concepts reported for the HAZARD model of Teuscher, Sabnis and Drivas (1983), and JETLEK extends the ONDLEK model of the US Coast Guard by Astleford, Morrow and Buckingham (1983) with its subsequent enhancements by Computer Data Systems (1985) and T.B. Morrow (1985).

29.24.6 PHAST

PHAST contains a suite of hazard models developed by DnV Technica, including TECJET, together with supporting facilities such as the DIPPR database.

29.25 Hazard Assessment Systems

The use of computer codes is virtually essential for a major probabilistic risk assessment and numerous in-house programs have been created. In the public domain, however, there are relatively few comprehensive codes available.

Table 29.14 lists some of the principal codes. Some of these codes are essentially complete quantitative risk assessments. An account of several of these systems is now given.

29.25.1 SAFETI

One such system is the SAFETI code developed by Technica for the Dutch Ministry of Housing, Physical Planning and Environment. This is a major code for the conduct of a complete probabilistic risk assessment (PRA). The development of the code was prompted by the Rijnmond PRA described in Appendix 8.

Accounts of SAFETI are given by Ale and Whitehouse (1986) and Pitblado and Nalpanis (1989). The program performs a complete PRA for a fixed installation. It is designed for ease of input, speed of processing and transparency of results, both intermediate and final. It is also designed for minimum loss of detail, and allows the level of detail to be varied.

Details of the plant are entered into the PLANT program. A plant is organized in terms of 'units' which are linked by connecting 'pipes' to 'vessels'. Vessels and pipes have associated with them a set of 'equivalent discrete failures' (EDFs), essentially leaks and ruptures. Each failure is assigned a failure frequency, for which default values are supplied. Other input information includes the population density, defined by a grid; the density of ignition sources; and the meteorological conditions. There are databases for the failure frequencies, population, ignition sources and meteorology.

A set of eight release scenarios is used. These are: (1) an instantaneous release (by vessel rupture) of a flammable material; (2) a continuous pressurized release (from vessel or pipe) of a flammable material; (3) the vaporization of a refrigerated flammable liquid; (4) a pool fire; (5) a fireball or BLEVE; (6) an instantaneous pressurized release (by vessel rupture) of a toxic material; (7) a continuous pressurized release (from vessel or pipe) of toxic material; and (8) the vaporization of a refrigerated toxic liquid. The program CONSEQ handles the development of these releases utilizing a set of four event trees, for which the starting events are one of the four possible combinations of instantaneous vs continuous and aerosol vs no aerosol in the cloud. The nodes in these event trees include the following queries: (1) Rainout? (2) Evaporation? (3) Pool left behind? (4) Pool of limited duration? (5) Essentially instantaneous? (6) Behaves as a free jet?

The hazard models used are described in Chapter 9. There are four gas dispersion models together with a set of models for vaporization from a pool, jet flames, fireballs, BLEVEs and vapour cloud explosions and probit equations for injury and damage.

The outcomes of the event trees for flammable releases are events which are then modelled, using the set of hazard models and probit equations, in the program IMPACT. The results can be output in a variety of forms, including as risk contours, individual risks and frequency–number curves.

There are interactive facilities which permit the user to: bypass some or all of the automatic generation of EDFs and to replace them with alternative releases or events; replace a default failure frequency with an alternative value; and replace a standard hazard model with an alternative one.

The version of SAFETI just described is the original, classic one. There are in fact three versions: SAFETI Classic, SAFETIMicro and SAFETIToolkit. The latter incorporates engineering from the offshore toolkit OHRAT.

29.25.2 WHAZAN

A rather simple code is WHAZAN, developed by Technica for the World Bank. It is described in the *Manual of Industrial Hazard Assessment* (Technica, 1986). WHAZAN provides a facility for the user to explore the consequences of a set of release scenarios. The event tree for these scenarios was given in Figure 9.23. The core of the program is a set of hazard models. These models were given in Table 9.21. The program does not make estimates of the frequency of the scenarios or of the risks. WHAZAN is a much more modest package than SAFETI and was developed to run on a PC in the first instance.

29.25.3 RISKAT

The HSE has developed its own hazard assessment program entitled initially the Risk Assessment Tool (RAT), and latterly RISKAT. Accounts have been given by Pape and Nussey (1985), Crossthwaite, Fitzpatrick and Hurst (1988), Hurst, Nussey and Pape (1989) and Nussey, Pantony and Smallwood (1992). The essential features of this program have been described in Chapter 9 in connection with the HSE guide assessments for liquefied petroleum gas and chlorine.

29.25.4 PRAM

The pipeline risk assessment method (PRAM) of the HSE is encoded in a suite of programs, as described by D.A. Carter (1991). PROFIT calculates the emission flow from the pipeline. Two scenarios are then considered. The first is that the leak ignites and gives a jet flame, and the second is that the gas disperses and then ignites. For the first scenario, SHELF calculates the size and other properties of the jet flame and MAJESTIC the thermal dose received by the target. For the second scenario, DISPI calculates the probability that a stationary target is within the envelope of the flammable part of the cloud.

29.25.5 TRANSPIRE

A hazard assessment system for pipelines, TRANSPIRE has been developed by British Gas (Hopkins, 1993; Hopkins, Lewis and Ramage, 1993). The constituent programs include: FFREQ, for failure rates of pipelines due to third party interference; PIPEBREAK, for gas emission rates; FRACTURE1, for the fire from a full line rupture; THORIN, for the fire from a puncture of the line; JINX2, for the dispersion of a gas jet; DESC2, for the damage and injury effects of time-varying thermal radiation; and WINSR2, for individual and societal risk.

29.25.6 Safety Case Manager

Safety Case Manager (AEA Technology) is a multi-media tool for the handling of safety cases.

29.26 Plant Operation

29.26.1 Data reconciliation

Programs for reconciliation of measured data from the plant, to obtain more accurate mass and heat balances, etc., include:

AutoPLANT Data (ESD)
IBIS (CESS)
RAGE (Engineers India)
RECONSET (CESS)

29.27 Transport

Hazard assessment systems for transport are not well represented, but one such is the Transportation Risk Screening Program of A.D. Little, which supports evaluation of the risks from different chemicals, transport modes and routes.

29.28 Emergency Planning

29.28.1 Emergency response systems

There are several packages for the simulation in real time of the development of an emergency using suitable hazard models. The essential concept is that in an emergency the system is provided with certain key pieces of information, such as the material released, estimates of the location and size of the leak and the meteorological conditions, and gives a VDU display of the phenomenon such as plan and elevation contours of gas concentration.

One such system is SAFER (Dupont Safer Emergency Systems). The core of the code is a gas dispersion program together with data on the chemicals handled in the plant and their properties. The computer is provided with a network of instruments which measure meteorological conditions such as wind direction and speed. In an emergency, data are furnished to the computer both by these instruments and by operator inputs. SAFER is more than a computer code. It is essentially an emergency response system built around the computer package. SAFER is described by Gelinas (1985) and Hughson (1991a).

Other real-time emergency information systems are:

CHARM (Radian Corp.)
CHIEF (Westinghouse)
DISCOVER (ICI)
PlantSafe (Environmental Response Systems)

DISCOVER has been described by Preston (1993, 1994).

Plate 19 shows a display obtained on the DISCOVER system and Plate 20 shows some displays on the SAFER system.

Further accounts of emergency response packages include those of Hesel and Schnadt (1982), Lashover (1985), Stern (1986), Egol (1989a) McPherson (1989) and Hughson (1991a). Zannetti (1990) lists a large number of other computer codes with various degrees of application to emergency planning.

29.28.2 Emergency simulation

An aid to training personnel in the handling of emergencies is available in the form of the HANDLING EMERGENCIES simulation system of the IChemE. The trainee assumes the role of the main incident controller and is responsible for controlling all personnel and issuing operational commands. The program contains nine incident scenarios involving fire, toxic release and a combination of both. It uses a pre-plan entered by the trainee to determine how the scenario develops. The scenario highlights weak points in the pre-plan. In order to assist post-mortem analysis, a log is provided of events during the incident and of actions taken.

29.29 Environment

29.29.1 Flowsheet simulation

An environmental simulation program is available in ESP from Davy Energy and Environment, which is based on the earlier PROCHEM code and permits the simulation of a process with respect to its environmental features. It includes a properties database, a properties estimation facility, a database of treatment processes, steady-state and dynamic process simulators, models of treatment operations and models of the fate of chemicals in the environment.

29.29.2 Fugitive emissions

A particular aspect of environmental impact is fugitive emissions of volatile organic compounds. Some programs which estimate such emissions are:

CHEMCALC 17 and 18 (Gulf)
Emission Master (Mitchell Engineering)
TTKEM (Tees Engineering)

29.29.3 Environmental fate databases

Information on the environmental fate of chemicals is available in the following databases:

ENVIROFATE (CIS)
Environmental Fate Database (Technical Database Services)

29.29.4 Environmental models

The airborne dispersion of chemicals in the environment is modelled using the gas dispersion codes described in Section 29.21. Models for other modes include:

HSPF (EPA) Waterborne dispersion
PRAIRIE River dispersion and pollution
WASP 4 (EPA) Surface water dispersion

29.30 Offshore

Many of the computer codes already described are relevant to offshore situations. The account given in this section is confined to programs developed specifically for offshore work.

29.30.1 Reliability databases

The OREDA offshore reliability database, described in Appendix 14, is available on computer.

29.30.2 Pipeline and well flows

There are a number of programs developed to support the pumping of offshore fluids through pipelines, including codes for multi-phase flow in pipelines:

ASAPIPE (ASA)
PIPESIM (Baker Jardine)

and for flow in wells:

ASAWELL (ASA)

29.30.3 Ship–platform collision

The CRASH code (DnV Technica) provides a method of assessing the risk of collision between a ship and an offshore installation.

29.30.4 Explosion modelling

Many of the computational fluid dynamics codes such as FLACS and CLICHE have found much of their application offshore. Heavy gas dispersion codes have also been applied to offshore problems.

29.30.5 Blast resistance

As part of its programme of work on fire and explosion on offshore platforms, the HSE has reviewed codes for the response of offshore structures to blast loading. This review is given in *Computerized Analysis Tools for Assessing the Response of Structures Subjected to Blast Loading* (HSE, 1992 OTI 92 601).

The review deals essentially with finite element (FE) and simplified techniques for the structural response to blast. It discusses the types of analysis required: static vs dynamic and linear vs non-linear. It also considers the types of failure of interest: premature failure and total collapse. It shortlists a number of FE programs suitable for assessing the response of structures such as three-dimensional beams, plates and cylinders. Some of these codes were originally developed for defence purposes, others are general. The codes shortlisted include:

ABAQUS (SDRC-CAE Int.)
ASAS-NI (WS Atkins)
(AUTDYN (WS Atkins)
(DYNA-3D (LLNL)
(OASYS DYNA-3D (Pafec)

29.30.6 Hazard model systems

A suite of hazard models for fire and explosion events on offshore platforms is contained in CHAOS, developed by British Gas. The models cover gas build-up, explosion loading and response, and fire loading and response.

29.30.7 Hazard assessment systems

There are a number of hazard assessment codes which have been developed with an orientation to offshore work or adapted to such work. Mention has already been made of PLATO, which handles the escalation of initial events in a manner more convenient than the conventional event tree method. PLATO constitutes in effect a complete hazard assessment system. Another hazard assessment tool is OHRAT, which is now described.

29.30.8 OHRAT

The Offshore Hazard and Risk Analysis Toolkit (OHRAT) (Technica, 1991) is a hazard assessment system developed by DnV Technica for use offshore. It has a structure specifically adapted to offshore events and contains a large number of hazard models for such events.

29.30.9 Evacuation, escape and rescue

Another suite of programs from DnV Technica are the codes for evacuation, escape and rescue. ESCAPE deals with the evaluation of survival craft availability, MUSTER simulates the mustering of personnel in an emergency and RESCUE simulates the rescue of personnel from the water by fast rescue craft.

29.31 Nuclear Industry

The nuclear industry has developed a large number of computer codes. Among the topics which these codes address are: the various aspects of probabilistic safety assessment, including fault tree and event tree analysis; thermal hydraulic analysis; and reactor accidents. Nuclear codes on these and other topics are listed in Appendix 28 and many are referred to elsewhere in this chapter.

29.31.1 Probabilistic safety assessment

The nuclear industry has a strong interest in probabilistic safety assessment. Many of the codes mentioned in Section 29.18 were originally developed for that industry. A review of such codes is given in *Computer Codes for Level I Probabilistic Safety Assessment* (IAEA, 1990). Level 1 of the PSA addresses the development of an incident prior to the loss of containment. The document gives lists of codes similar to those in Tables 29.5–29.8.

29.31.2 Thermal hydraulic transients

Codes on thermal hydraulic transients include the various versions of COBRA, COMMIX, MOD, RELAP and TRAC. Codes for nuclear reactor accidents include the versions of CONTAIN, CRAC, MACCS and MELCOR.

30 Artificial Intelligence and Expert Systems

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30.45 Fault Administration 30/100
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This chapter deals with artificial intelligence, expert systems and certain other advanced developments in computer aiding. The aim of the chapter is to provide an overview of the field and an appreciation of the sorts of problem which are tackled, the types of technique developed, the terminology used and the applications made.

Accounts of artificial intelligence (AI) include *Artificial Intelligence* (Winston, 1984), *Introduction to Artificial Intelligence* (Charniak and McDermott, 1985), *Introduction to Knowledge Based Systems* (Frost, 1986), *Introduction to Artificial Intelligence and Expert Systems* (Patterson, 1990), *The Elements of Artificial Intelligence* (Tanimoto, 1990) and *Encyclopaedia of Artificial Intelligence* (Shapiro, 1992).

An important area of AI is expert systems. A large proportion of the AI applications in the process industries are of this nature. Expert systems are therefore given particular attention in this chapter.

Most accounts of AI are written in a style which makes extensive use of lines or sections of computer programs. For the most part this practice has not been adopted here. The aim has been to couch explanations in natural language. Some limited use has been made of program-type material, however, purely in order to give a feel for the approaches taken. The expressions principally used are related to the predicate calculus. This has influenced the order of treatment of the subjects in the chapter. The account of programming languages is placed after the account of predicate logic but before most of the other topics where program-type material may be used.

Selected references on AI and on expert systems are given in Table 30.1.

Table 30.1 *Selected references on artificial intelligence, expert systems and advanced aids*

A General

Hempel (1952); Craik (1943); Bruner, Goodnow and Austin (1956); Vickers (1968); Simon (1969); Lindsay and Norman (1972); J. Anderson and Bower (1973); Schank and Colby (1973); Bobrow and Collins (1975); J. Anderson (1976); Weizenbaum (1976); Sternberg (1982); Schon (1983)

Artificial intelligence
Bowden (1943); Turing (1950, 1963); Feigenbaum and Feldman (1963); Newell and Simon (1963, 1972); Minsky (1967); Ernst and Newell (1969); Findler and Meltzer (1971); Nilsson (1971, 1980); Lighthill (1973); Michie (1974, 1982a,b,d, 1983); E.B. Hunt (1975); Rubin (1975); Raphael (1976); Boden (1977); Winston (1977); Latombe (1978); Feigenbaum (1979, 1983); N. Graham (1979); Nii and Aiello (1979); Charniak, Riesbeck and McDermott (1980); Barr and Feigenbaum (1981–); Schank and Riesbeck (1981); P.R. Cohen and Feigenbaum (1982); Szolovits (1982); Feigenbaum and McCorduck (1983); Hayes and Michie (1983); Michalski, Carbonnell and Mitchell (1983); Rich (1983); Durham (1984b); O'Shea and Eisenstadt (1984); Reitman (1984); Simons (1984, 1988); Sowa (1984); Winston and Prendergast (1984); Charniak and McDermott (1985); P.R. Cohen (1985); Hillman (1985); J.J. Richardson (1985); Shirai and Tsujii (1985); Frost (1986); Kanal and Lemmer (1986); C. Williams (1986); Yazdani (1986); Gevarter (1987); Cleal and Heaton (1988); Ramsay and Barret (1987); Jezzard (1988); Savory (1988); W.A. Taylor (1988); Mirzai (1990); Patterson (1990); Tanimoto (1990); Martins (1992); Shapiro (1992)

Expert systems
Waterman and Hayes-Roth (1978); Chisholm and Sleeman (1979); Michie (1979, 1980, 1981, 1982a–d); Waterman (1979, 1981, 1985); Reboh (1980); Addis (1982); R. Davis (1982); R. Davis and Lenat (1982); Sacerdoti (1982); Stefik *et al.* (1982); Bigger and Coupland (1983); Bramer (1983, 1984); Duda and Shortliffe (1983); Hayes-Roth, Waterman and Lenat (1983); Naylor (1983); Stefik and de Kleer (1983); Swartout (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); Alvey, Myers and Greaves (1984); V. Begg (1984); Durham (1984a, 1985a); Forsyth (1984a,b); R. Brown (1985); A. Goodall (1985); Gupta, Bandler and Kiszka (1985); Harmon and King (1985); Hayes-Roth (1985); Michaelson, Michie and Boulanger (1985); Mill (1985); Politakis (1985); Sell (1985): Denning (1986); Dreyfus and Dreyfus (1986); Elliot (1986); Frost (1986); S. Hughes (1986); Keravnou and Johnson (1986); L. Moskowitz (1986); Myers (1986); S. Wood (1986); Hu (1987); Kerridge (1987); Quinlan (1987); Shapiro (1987); Slatter (1987); Sturridge (1987); Cleal and Heaton (1988); Evitt and Mukaddam (1988); A. Goodall (1988); Greenwell (1988); Huang and Fan (1988); Ince (1988); Madni (1988); J. Martin and Oxman (1988); Parsaye and Chignell (1988); Pham (1988); Savory (1988); C. Tayler (1988b); Waters and Nielsen (1988); J.A. Campbell and Cuena (1989); Lien (1989); Madhavan and Kirsten (1989); Vadera (1989); Ferrada and Holmes (1990); IEE (1990 Conf. Publ. 322, 1991 Coll. Dig. 91/26); Patterson (1990); Ford (1991); Mitter (1991); Gonzales and Dankell (1993)

Knowledge acquisition
R. Davis (1977, 1978); Waterman (1978, 1981); Chisholm and Sleeman (1979); Nilsson (1980); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Sell (1985); Boose (1986); Kidd (1987); Chignell and Petterson (1988); Norman and Naveed (1988); Diaper (1989); Aldersey, Lees and Rushton (1993)

Knowledge representation
Michie (1974); Winograd (1975); Hayes (1977); Lyons (1977); Winston (1977); Barr and Feigenbaum (1981–); Culicover (1982); Hayes-Roth, Waterman and Lenat (1983); Israel (1983); Weiss and Kulikowski (1983); Simons (1984); Harmon and King (1985); Sell (1985); Beynon and Davies (1987); Hodgson (1991)
Language: Chomsky (1957); Winograd (1972, 1983); Lawson (1982); Pinker (1984); Cullingford (1986); J. Allen (1987)
Pattern recognition: Fu (1981)
Vision: H.C. Andrews (1970); Hanson and Riseman (1978); Ballard and Brown (1982); Marr (1982); Horn (1986)
Logic: Stebbing (1942); Lukasiewicz (1951); Suppes (1957); Kleene (1967); Ennis (1969); Nilsson (1971, 1980); Lemmon (1972); Manna (1973); Shafer (1976); van

Emden (1977); Hodges (1978); Kowalski (1979); R. Turner (1984)
Predicate calculus: Larson and Michalski (1977); Nilsson (1980); Clocksin and Mellish (1981); Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984)
Incidence calculus: Bundy (1984)
Heuristics: Polya (1954, 1957); Buchanan, Feigenbaum and Sridharan (1972); Wickelgren (1974); Sussman and Stallman (1975); Pearl (1984)
Procedural representation: Raphael (1968); Hewitt (1972)
Production systems, rules: Newell (1973); R. Davis and King (1976); R. Davis, Buchanan and Shortliffe (1977); Winston (1977); Waterman and Hayes-Roth (1978); van Melle (1979); Nilsson (1980): Barr and Feigenbaum (1981–); Winston and Horn (1981); Alty and Coombs (1984); Simons (1984); Harmon and King (1985); Sell (1985)
Semantic networks: Minsky (1968); J. Anderson and Bower (1973); Simmons (1973); Michie (1974); Norman and Rumelhart (1975); Winston (1977, 1984); Duda *et al.* (1978); Chisholm and Sleeman (1979); Rychener (1979); Nilsson (1980); Barr and Feigenbaum (1981–); Alty and Coombs (1984); Simons (1984); Harmon and King (1985); Sell (1985)
Semantic primitives: Wilks (1975); Schank and Abelson (1977); Winograd (1978)
Frames: Kuipers (1975); Minsky (1975); Bobrow and Winograd (1977); Schank and Abelson (1977); Winston (1977, 1984); Barr and Feigenbaum (1981–); Winston and Horn (1981); Alty and Coombs (1984); Harmon and King (1985)
Bayesian logic: Duda, Hart and Milsson (1976); Naylor (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); Sell (1985)
Fuzzy logic: Zadeh (1965, 1968, 1975a,b, 1978, 1979, 1983a,b, 1985, 1992); Zadeh and Fukanaka (1975); Gaines (1976); Gaines and Kohout (1977); Dubois and Prade (1980); Mamdani and Gaines (1981); Forsyth (1984c); Kacprzyck (1983, 1992); Zimmerman (1984, 1986, 1987); di Nola *et al.* (1989); Zadeh and Kacprzyck (1992)
Odds: Michie (1982a)

Operation, control, search
Control strategies: Winston (1977, 1984); R. Davis (1980a,b); Nilsson (1980); Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984); Harmon and King (1985); Sell (1985)
Search: Doran and Michie (1966); Doran (1968); Michie (1974, 1982b); Winston (1977, 1984); Charniak, Riesbeck and McDermott (1980); Nilsson (1980); Barr and Feigenbaum (1981–); Gardner (1981); Winston and Horn (1981); Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984); Simons (1984); Montgomery (1991)
Forward chaining, backward chaining, backtracking: Charniak, Riesbeck and McDermott (1980); Nilsson (1980); Winston and Horn (1981); Weiss and Kulikowski (1983); Alty and Coombs (1984); Winston (1984); Harmon and King (1985)
Inference engine: Hayes-Roth, Waterman and Lenat (1983); Naylor (1984)

Problem-solving
Games and puzzles: Michie (1974)
Draughts (checkers) and chess: C.E. Shannon (1950a,b); Newell, Shaw and Simon (1958); Samuel (1959, 1960, 1963a,b, 1968); Michie (1974); Newborn (1975); Shapiro and Niblett (1982)
Theorem-proving: C.C. Green (1969); Michie (1974)
GPS: Newell, Shaw and Simon (1960); Newell and Simon (1963); Ernst and Newell (1969)

Facilities
Blackboard systems: Engelmore and Morgan (1988)
Questioning, questionnaires: Weiss and Kulikowski (1983)
Explanation: A.C. Scott *et al.* (1977); W.J. Clancey (1979, 1983); Hayes-Roth, Waterman and Lenat (1983); Sell (1985); Ellis (1989)

Learning
Nilsson (1965, 1988); Michie (1974, 1983); D. Shaw, Swartout and Green (1975); Summers (1977); Winston (1980, 1982, 1984); Dietterich and Michalski (1981); Simon (1983); Forsyth (1984d); Hart (1984); Simons (1984); S.F. Smith (1984); Durham (1985d,e); M. James (1985); Schlimmer and Langley (1992); Al-Attar and Hassan (1994); C.C. Taylor, Spiegelhalter and Michie (1994)
ID3: Quinlan (1979, 1983a,b); Durham (1985d); Quinlan *et al.* (1986)

Planning
Fikes and Nilsson (1971); Fikes, Hart and Nilsson (1972); Sacerdoti (1975, 1977); Stefik (1981a,b); Vere (1983, 1992); Oshima (1983); Wilensky (1983); Chapman (1985); J. Allen, Hendler and Tate (1990); Lyons and Hendricks (1992)

Tutoring
Sleeman and Brown (1982)

Validation
Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); A. Stevens (1984); Sell (1985)

Programming
Knuth (1968, 1969, 1973); Tyugu (1988)
Compilation, compilers: Bornat (1979); Charniak, Riesbeck and McDermott (1980)
List processing: Forster (1967)
Logic programming: Kowalski (1974, 1979); van Emden (1977); J.A. Robinson (1979, 1983); K.L. Clark and Tarnlund (1982); K.L. Clark (1983); Oliviera (1984); Sell (1985); Amble (1987)
Recursion: Burge (1975); Winston and Horn (1981)

Languages
LISP: McCarthy *et al.* (1962); Weissman (1967); D.P. Friedman (1974); Siklossy (1976); Winston (1977); J. Allen (1978, 1979); McCarthy (1978); Pratt (1979); Charniak, Riesbeck and McDermott (1980); Barr and Feigenbaum (1981–); Teitelman and Masinter (1981); Winston and Horn (1981); Danicic (1983); Gnosis (1984); Hasemer (1984a,b); Laubsch (1984); Queinnec (1984); Steel (1984); Harmon and King (1985); Narayanan and Sharkey (1985); Coxhead (1987)
PROLOG: Kowalski (1974, 1979); van Emden (1977); Warren, Perreira and Perreira (1977); Coelho *et al.*

(1980); Clocksin and Mellish (1981); K.L. Clark and McCabe (1982); J.A. Campbell (1983, 1984); Mizoguchi (1983); Swinson (1983); Alty and Coombs (1984); Clocksin (1984); Forsyth (1984a); Li (1984); Schlobohm (1984); Yazdani (1984, 1985); Burnham and Hall (1985); J. Cohen (1985); Colmerauer (1985); Durham (1985c); Harmon and King (1985); de Saram (1985); Hinde (1986); Sterling and Shapiro (1986); Saint-Dizier (1987)
POP-2: Popplestone (1967); Burstall (1971); Burstall and Collins (1971); Burstall and Popplestone (1971); Burstall, Collins and Popplestone (1971)
POP-11: Ramsay and Barrett (1987); Popplestone (1992b)
POPLOG: Sloman, Hardy and Gibson (1983); Hardy (1984); Popplestone (1992a)
Object-oriented programming: Goldberg and Robsen (1983); B.J. Cox (1986); Stefik and Bobrow (1986); S. Cook (1987)
C++: Coplien (1992); Wang (1994)

Example systems
DENDRAL: B.G. Buchanan, Sutherland and Feigenbaum (1969, 1970); Feigenbaum, Buchanan and Lederberg (1971); Michie (1974); B.G. Buchanan *et al.* (1976); Carhart (1977); B.G. Buchanan and Feigenbaum (1978); B.G. Buchanan (1979); Nilsson (1980); Lindsay *et al.* (1980); Barr and Feigenbaum (1981–); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); B.G. Buchanan and Shortliffe (1984); Winston (1984); Harmon and King (1985); Sell (1985)
PROSPECTOR: Duda *et al.* (1978); Hart, Duda and Einaudy (1978); Duda, Gaschnig and Hart (1979); Reboh (1980, 1981); Barr and Feigenbaum (1981–); Duda and Gaschnig (1981); A. Campbell *et al.* (1982); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); Harmon and King (1985); Sell (1985)
MYCIN: Shortliffe and Buchanan (1975); Shortliffe (1976); W.J. Clancey, Shortliffe and Buchanan (1979); Shortliffe, Buchanan and Feigenbaum (1979); Barr and Feigenbaum (1981–); W.J. Clancey and Lettsinger (1981); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); Cendrowska and Bramer (1984); Winston (1984); Harmon and King (1985); Sell (1985)
TEIRESIAS: Barr and Feigenbaum (1981–); Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984); Winston (1984)
R1, XCON, XCEL: McDermott (1980, 1981, 1982a,b); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984); Bachant and MacDermott (1984); Kraft (1984); Winston (1984); Harmon and King (1985); van de Brug, Bachant and MacDermott (1986); Durham (1987)
CASNET: Weiss, Kulikowski and Safir (1977, 1978); Weiss *et al.* (1978); Barr and Feigenbaum (1981–); Weiss and Kulikowski (1981, 1983); Kulikowski and Weiss (1982); Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984)
MOLGEN: Hayes-Roth, Waterman and Lenat (1983); Alty and Coombs (1984)
INTERNIST: R.A. Miller, Pople and Myers (1982); Pople (1982)
PUFF: Hayes-Roth, Waterman and Lenat (1983); Naylor (1983)
OPS: Forgy and McDermott (1977); Forgy (1981); Hayes-Roth, Waterman and Lenat (1983); Brownston *et al.* (1985); Harmon and King (1985)
KAS: Hayes-Roth, Waterman and Lenat (1983); Harmon and King (1985)
Spill prevention: B.A. Kelly and Oakes (1980); Hayes-Roth, Waterman and Lenat (1983)
AL/X: Reiter (1980)
STEAMER: Holan, Hutchings and Weitzman (1984)
AM EURISKO: Lenat (1982, 1983); Lenat and Brown (1984); Durham (1985f)

Shells
Cendrowska and Bramer (1984); E.J. Miller, Wilson and Lewis (1988)
EMYCIN: van Melle (1979, 1980, 1981); van Melle, Shortliffe and Buchanan (1981); Hayes-Roth, Waterman and Lenat (1983); Weiss and Kulikowski (1983); Alty and Coombs (1984)
EXPERT: Weiss and Kulikowski (1979, 1981); Barr and Feigenbaum (1981–); Kulikowski and Weiss (1982); Hayes-Roth, Waterman and Lenat (1983); Harmon and King (1985)
MICRO EXPERT: P. Cox (1984)
ES/P ADVISOR: Harmon and King (1985)
CRYSTAL: Wallsgrove (1988)
G2: Gensym Corp. (1992)

Databases
Date (1977); R. Davis (1980); Ullman (1982); Maier (1983); Frost (1986)

Decision aids
Kunz and Rittle (1970); Conklin and Begeman (1988); Potts and Bruns (1988); Lubers (1991)

Documentation aids
Bourdeau (1991); Kahkonen and Bjork (1991); Casson (1992); Casson and Stone (1992); Chung and Stone (1994)

Neural networks
Minsky and Papert (1969); Touretszky and Hinton (1985); Gallant (1988); Saito and Nakano (1988); IEE (1989 Conf. Publ. 313, 1991 Conf. Publ. 349, Coll. Dig. 91/19, 1993 Conf. Publ. 372); Beale and Jackson (1990); Zeidenberg (1990)

B Process applications

Engineering design
Simon (1969); P. Freeman and Newell (1971); Eastman (1978); D.C. Brown and Chandrasekaran (1989); Ganeshan, Finger and Garrett (1991)

Artificial intelligence
Chowdhury and Caudwell (1982); F. Kane (1986); Stephanopoulos (1990); Bunn and Lees (1988); Hutton, Ponton and Waters (1990)

Expert systems
Anon. (1984tt); Andow (1984); B. Knight *et al.* (1984); Anon. (1985l); Banares-Alcantara and Westerberg (1985);

Banares-Alcantara, Westerberg and Rychener (1985); Avni, Kandell and Gupta (1985); Baker-Counsell (1985b); Banares-Alcantara, Sriram *et al.* (1985); Berkovitch and Baker-Counsell (1985); Chowdhury (1985b); Chowdhury, Short and Gibb (1985); M. Henry (1985); R.L. Moore (1985); Sachs, Paterson and Turner (1985); Voller and Knight (1985); Anon (1986h); Basden and Hines (1986); Beazley (1986); British Gas (1986 Comm. 1297); Branch (1986); Coulsey (1986); Durham (1986); Ferguson and Andow (1986); Hines (1986); Hines and Basden (1986); Hollnagel *et al.* (1986); R.A. King (1986); Kosar and Blahut (1986); Niida *et al.* (1986); Shirley and Fortin (1986); Vaija, Jarvelainen and Dohnal (1986b); Anon. (1987k,s); Andow and Ferguson (1987); N. Atkinson (1987a); Banares-Alcantara *et al.* (1987); Barnwell and Ertl (1987); Holt *et al.* (1987); IBC (1987/71); A. Moore (1987); Oxman and Gero (1987); Rafaat and Abdouni (1987); Rand (1987); Russo and Peskin (1987); Sangiovanni and Romans (1987); Shirley (1987); Stephanopoulos (1987); Tayler (1987b); Anon. (1988n); Banares-Alcantara, Ko *et al.* (1988); Birky, McAvoy and Modares (1988); Bunn and Lees (1988); Norman and Naveed (1988); Novak, Schechter and Lake (1988); Royse (1988); Shum *et al.* (1988); W.A. Taylor (1988); BRE (1989 IP4/89); Gani (1989); Hofmeister, Halasz and Rippin (1989); Hollnagel (1989); Lahdenpera, Korhonen and Nystrom (1989); Birky and McAvoy (1990); Suokas, Heino and Karvonen (1990); Gulbrandsen (1991); Leicht, Wingender and Ruppert (1991); Quantrill and Liu (1991); Calzada, Espasa and Barrera (1992); Crowe *et al.* (1992); Fiumi and Giorgio (1992); Hanratty and Joseph (1992); Martinez *et al.* (1992); Samdani and Fouhy (1992); Chang, Hwang and Hwang (1993); Hingoraney (1994)

Process plant design, equipment selection
Rudd and Watson (1968); Bunn and Lees (1988); Myers, Davis and Herman (1988); Waters, Chung and Ponton (1989); Waters and Ponton (1992); Chung, Abbas and Robertson (1993); Yang *et al.* (1993)

Process modelling
Franks (1967); Durham (1985b); A.R. Mitchell and Griffiths (1980); Andersson (1989); Cott *et al.* (1989); Nilsson (1989); Piela *et al.* (1991); Gallun *et al.* (1992); Marquardt (1992); Nemeth *et al.* (1992)

Process synthesis
Powers and Jones (1973); May and Rudd (1976); Westerberg (1980, 1985, 1989); Nishida, Stephanopoulos and Westerberg (1981); Umeda (1982); Rippin (1983); Sargent (1983); Stephanopoulos (1983); Grossman and Floudas (1987); Grossman, Westerberg and Biegler (1987); Montagna *et al.* (1987); Pai and Hughes (1987); Beltramini and Motard (1988); Douglas (1988); Floquet, Piboleau and Domenech (1988); Kirkwood, Lock and Douglas (1988); Reklaitis and Spriggs (1988); Engelmann *et al.* (1989); Grossman (1989); Hofmeister, Halasz and Rippin (1989); Motard (1989); Mizsey and Fonyo (1990); Ostrovsky and Berezinsky (1991); Raman and Grossman (1991); Crowe *et al.* (1992); Journet (1993)

DESIGN-KIT
Stephanopoulos, Johnston *et al.* (1987)

MODEL.LA
Stephanopoulos, Hanning and Leone (1990a,b)

Planning
Rivas and Rudd (1974); Rivas, Rudd and Kelly (1974); Fusillo and Powers (1987, 1988a,b); Stephanopoulos *et al.* (1987); Foulkes *et al.* (1988); Lakshmanan and Stephanopoulos (1988a,b, 1990); Aelion and Powers (1991); Rotstein, Lavie and Lewin (1992); Soutter and Chung (1993)

Qualitative modelling
Andow (1973); Andow and Lees (1975); de Kleer (1975, 1984, 1985, 1992); Hayes (1979, 1985); Martin-Solis, Andow and Lees (1982); Gentner and Stevens (1983); de Kleer and Brown (1983, 1984, 1986); Wilensky (1983); Bobrow (1984, 1985); R. Davis (1984); Kuipers (1984, 1986, 1989); B.C. Williams (1984a,b); Hobbs and Moore (1985); Ponton and Vasek (1986); Weld (1987, 1988a,b); Dalle Molle, Kuipers and Edgar (1988); Mavrovouniotis and Stephanopoulos (1988); Oyeleye and Kramer (1988); Pethe, Singh and Knopf (1989); Waters and Ponton (1989); P. Rose (1990); Weld and de Kleer (1990); Yamashita, Shoji and Suzuki (1990); Catino, Grantham and Ungas (1991); Faltings and Struss (1991); Grantham and Ungar (1991); P. Rose and Kramer (1991); Hardt (1992); Koivisto *et al.* (1992); Fanti, Chung and Rushton (1993); Savkonic-Stevanovic (1994)

Order of magnitude estimation, modelling
Mosteller (1977) Mavrovouniotis and Stephanopoulos (1988)

Neural networks
Hoskins and Himmelblau (1988); Venkatasubramanian and King Chan (1989); Watanabe *et al.* (1989); Bhagat (1990); Bhat and McAvoy (1990); M.A. Kramer and Leonard (1990); Samdani (1990a); Venkatasubramanian, Vaidhyanathan and Yamamoto (1990); Okayama (1991); Venkatasubramanian and McAvoy (1992); Chitra (1993); Fan, Nikolaou and White (1993); A.J. Morris, Montague and Willis (1994)

Fault propagation
Andow (1973); Andow and Lees (1975); Umeda *et al.* (1979, 1980); Andow, Lees and Murphy (1980); Martin-Solis, Andow and Lees (1982); B.E. Kelly and Lees (1986a–d); Parmar and Lees (1987a,b); Khan and Hunt (1989); Waters and Ponton (1989); A. Hunt *et al.* (1993a–e)
QUEEN: Chung (1993)

Design decision aids
Ramirez-Dominguez and Banares-Alcantara (1993); Chung and Goodwin (1994); Goodwin and Chung (1994a,b)

Explosion venting
Santon *et al.* (1991); von Haefen (1992); Santon (1992)

Reliability engineering
FIABEX: M.M. Grant and Harvey (1989)

Hazard identification
Lihou, Rahimi and Fletcher (1980); Lihou (1983 LPB 51); Andow and Ferguson (1987); Karvonen, Suokas and Heino (1987); Kletz (1988b); Weatherill and Cameron (1988, 1989); N. Morgan (1992b); Heino, Suokas and

Karvonen (1989a,b); C. Price and Hunt (1991); C. Price *et al.* (1991); R.A. Freeman, Lee and McNamara (1992); Goring and Schecker (1992); Heikkila and Heino (1992); Heino, Poucet and Suokas (1992); Schönenburg (1992); Lear (1993); Heino *et al.* (1994); Venkatasubramanian and Vaidhyanathan (1994)
COMHAZOP: Rootsaert and Harrington (1992)
HAZID: Parmar and Lees (1987a,b); Zerkani and Rushton (1992, 1993)

Failure modes and effects analysis (FMEA)
C. Price *et al.* (1991)

Fault tree drafting and synthesis
W.Q. Smith and Lien (1968); Fussell (1973a,b); Henley (1977); L.S. Baker *et al.* (1978); Camarda, Corsi and Trentadue (1978); D.J. Allen and Rao (1980); Lihou (1980b); Poucet and de Meester (1981); Amendola *et al.* (1983); Poucet (1983); D.J. Allen (1984); Shafaghi, Andow and Lees (1984); Shafaghi, Lees and Andow (1984); VTT (1985 Res. Rep. 330); Kumamoto and Henley (1986); Kohda and Henley (1988); Mullhi *et al.* (1988); Napier and Palmer (1988); de Vries (1990); Bossche (1991a–c); Chuei-Tin Chang and Her-Chuan Hwang (1992)
CAT: Salem, Apostolakis and Okrent (1975a,b, 1977); Chu (1976); Apostolakis, Salem and Wu (1978); Salem, Wu and Apostolakis (1979); Salem and Apostolakis (1980); Squellati (1980); Poucet (1983)
FAULTFINDER: Andow and Lees (1975); Martin-Solis, Andow and Lees (1977, 1980, 1982); B.E.Kelly (1982); B.E. Kelly and Lees (1986a–d); Mullhi *et al.* (1988); A. Hunt *et al.* (1993a–e)
FTS: Powers and Tompkins (1974a,b, 1976); Powers and Lapp (1976, 1977); Henley and Kumamoto (1977); Lapp and Powers (1977a,b, 1979); Locks (1979, 1980); Powers (1977); Shaeiwitz, Lapp and Powers (1977); Lambert (1979); Yellman (1979); Cummings, Lapp and Powers (1983)
RIKKE: J.R. Taylor (1982); J.R. Taylor and Olsen (1983); J.M. Morgan (1985)

Hazard models
Rao and Raj (1990); Koivisto *et al.* (1991)

Hazard assessment
Nelms (1988); Jäger, Diedershagen and Kühnreich (1989); Reeves and Mennell (1989); Reeves, Wells and Linkens (1989); Kakko (1991); Heino, Poucet and Suokas (1992)

Process monitoring
Stainthorp and West (1974); Hogger (1975); Berenblut and Whitehouse (1976, 1977); Anon. (1977a); Munday (1977); Dye (1979); Cheung and Stephanopoulos (1990); Alty and McCartney (1991); Alty and Bergan (1992)
RESCU: Shorter (1985)

Multi-media systems
Alty and McCartney (1991); Alty and Bergan (1992); Tani *et al.* (1992)

Fault administration and diagnosis
Jervis and Maddock (1965); Welbourne (1965, 1968, 1974); Kay (1966); Kay and Heywood (1966); Barth and Maarleveld (1967); Patterson (1968); Andow (1973, 1982, 1984, 1985a–c, 1986); E. Edwards and Lees (1973, 1974); Andow and Lees (1975); Dahll (1976); Dahll *et al.* (1976); Powers and Lapp (1977); EPRI (1978 EPRI NP-613, 1980 EPRI NP-1379, EPRI NP-1684); Frogner and Meijer (1978, 1980); Iri *et al.* (1979); Umeda *et al.* (1979); Gesellschaft für Reaktorsichheit (1980); Long (1980); Long *et al.* (1980); Meijer, Frogner and Long (1980); Lees (1981a, 1983c, 1984); Pau (1981a,b); Martin-Solis, Andow and Lees (1982); W.R. Nelson (1982, 1984); Kokawa, Miyaki and Shingai (1983); Guarro and Okrent (1984); Herbert (1984); Iserman (1984); Watanabe and Himmelblau (1984); W.R. Nelson and Blackman (1985); Shiozaki *et al.* (1985); Tsuge *et al.* (1985); Ungar (1985); Modarres and Cadman (1986); Rowan (1986); Wollenberg (1986); Arendt *et al.* (1987); Dalle Molle and Himmelblau (1987); Frank (1987); M.A. Kramer (1987a,b, 1988); Kumamoto and Henley (1987); Washio, Kitamura and Sugiyama (1987); Ramesh, Shum and Davis (1988); Rich and Venkatasubramanian (1988, 1989); Shum *et al.* (1988); Venkatasubramanian (1988); Venkatasubramanian and Rich (1988); B. Chen *et al.* (1989); Gertler and Qiang Luo (1989); M.A. Kramer and Finch (1989); Rich *et al.* (1989); Sang Hoon Han *et al.* (1989); Tsuge, Matsuyama and McGreavy (1989); Venkatasubramanian and King Chan (1989); Basila, Stefanek and Cinar (1990); L.W. Chen and Modarres (1990); Chung-Chen Chang and Cheng-Ching Yu (1990); D.J. Cooper and Lalonde (1990); Finch, Oyeleye and Kramer (1990); M.A. Kramer and Leonard (1990); Labadibi (1990); Poucet (1990); Qian (1990); P. Rose (1990); Trenchard (1990); Ungar, Powell and Kamens (1990); Venkatasubramanian, Vaidhyanathan and Yamamoto (1990); Yamashita, Shoji and Suzuki (1990); Adamson and Roberge (1991); Aldersey, Lees and Rushton (1991); Chen-Ching Yu and Chyuan Lee (1991); Hoskins, Kaliyur and Himmelblau (1991); Li and Olson (1991); McDowell and Davis (1991); Pelti, Klein and Dhurjati (1991); P. Rose and Kramer (1991); Yoon, Oh and Yoon (1991); Corea, Tham and Morris (1992); Corti and Sansone (1992); IEE (1992 Coll. Dig. 92/45, 92/48); Karvonen *et al.* (1992); Labadibi and McGreavy (1992); Ramesh, Davis and Schwenzer (1992); Saelid, Mjaavatten and Fjalestad (1992); Venkateswarlu, Gangiah and Rao (1992); Yih-Yuan Hsu and Cheng-Chin Yu (1992); Chuei-Tin Chang *et al.* (1993); Fan, Nikolaou and White (1993); Fathi, Ramirez and Korbicz (1993); Ramanathan, Kannan and Davis (1993)
Instrument system design: Lambert (1977); Plamping and Andow (1983); Plamping (1986); Ali and Narasimhan (1993)
ANTICIPATOR: Munday (1977); Dye (1979)
AUTOPES: Wagenaar, Boesmans and Schrijnen (1989)
COGSYS: Anon (1988n)

Malfunction detection
Instruments: Kuehn and Davidson (1961); Clementson (1963); Ripps (1965); Barton *et al.* (1970); Anyakora (1971); Goldmann and Sargent (1971); Sommer *et al.* (1971); Umeda, Nishio and Komatsou (1971); Anyakora and Lees (1972b, 1973); Nogita (1972); E. Edwards and Lees (1973, 1974); Nogita and Uchiyama (1973); R.N. Clark, Fosth and Walton (1975); Hawickhorst (1975); Bellingham (1976); Bellingham and Lees (1976a,b, 1977a,b); Lees (1976d); Mah, Stanley and Downing (1976); Willsky (1976); Stanley and Mah (1977); Himmelblau (1978, 1979); Park and Himmelblau (1983,

1987); Narasimhan and Mah (1987); Jongelen, den Heijer and van Zee (1988); Tjoa and Bielger (1991); Whiteley and Davis (1992)
Plant equipment: Gallier (1968); Anyakora and Lees (1972b); Lees (1972); Whitman (1972); Collacott (1976b, 1977b); Himmelblau (1978); Dalle Molle and Himmelblau (1987); M.A. Kramer (1987b); M.A. Kramer and Palowitch (1987)

Data management and reconciliation
Romagnoli and Stephanopoulos (1981); Gorczynski (1985); Himmelblau (1985); Iordache, Mah and Tamhane (1985); Madron (1985); Heenan and Serth (1986); Seith and Heenan (1986); Rosenberg, Mah and Iordache (1987); Crowe (1988); R.J. MacDonald and Howat (1988); Chen-Shan Kuo, Tamhane and Mah (1990); May and Payne (1992); Rollins and Davis (1992, 1993); Verneuil, Pin Yang and Madron (1992); Leibovici, Verneuil and Pin Yang (1993); McMorris and Graveley (1993)

Operating procedures
Tomita, Hwang and Oshinma (1989)

Robots
R. Brooks (1986, 1989); Schoppers (1987)

Transport systems
Blümel and Schulz-Forberg (1989)

Accident databases
Koivisto, Vaija and Dohnal (1989)

30.1 Knowledge Representation

30.1.1 Knowledge

Knowledge is of many kinds and this is reflected in the forms of knowledge representation used.

One distinction commonly made is between data and information. Other distinctions made about knowledge are domain-independent vs domain-specific, exact vs fuzzy, and procedural vs declarative knowledge. Some types of knowledge include: facts; models; distinctions; relationships; constraints; procedures and plans; and rules-of-thumb, or heuristics.

The extent of the knowledge required varies greatly between problems. In certain limited worlds, such as the 'blocks world' extensively studied in AI, the world knowledge required is quite limited. In real-life, or mundane, situations on the other hand, the human comes to the problem possessed of a massive store of knowledge. He draws from this information not only about facts but also about other aspects such as constraints.

30.1.2 Natural language

By far the most widely used and most expressive form of knowledge representation is natural language. As a method of representation in AI work, however, natural language has a number of deficiencies.

There are a number of fundamental problems of natural language in this respect. It tends to be ambiguous. Its syntax and semantics are not well understood. There is considerable diversity in the structure of sentences. In some cases the meaning depends on the context.

Work in AI tends to involve the use of structured knowledge and natural language is not an obvious method for this purpose.

30.1.3 Databases

By contrast, in data bases structure is a principal feature of the knowledge representation. In large part this structure is oriented to data retrieval, but it may also represent relationships between the objects stored, and databases generally have certain facilities for certain elementary transformations on the data. Databases are considered further in Section 30.2.

30.1.4 Classical logics

Logic is a formal method of reasoning and provides a sound theoretical basis for the reasoning process. This is particularly important for computer-based approaches.

There are two principal logics in common use. One of these classical logics is propositional logic (PL) and the other first order predicate logic (FOPL). Propositional logic is the earlier form, is simpler and is generally the starting point in teaching.

Predicate logic has been developed to overcome some of the limitations of propositional logic. It is a more general logic of which propositional logic may be regarded as a special case. It is predicate logic which is most widely used in AI and which is used in 'logic programming'.

Propositional logic has a number of serious limitations. It cannot readily describe properties of entities or express relationships between them.

Predicate logic has been developed as a form of logic with enhanced expressiveness. It replaces propositions with predicates and utilizes functions, variables and quantifiers. This makes it possible to reason about entities in terms of their classes and of their relationships.

In defining the syntax of a logic use is frequently made of the Backus–Naur form (BNF).

Propositional logic and predicate logic are described in Sections 30.3 and 30.4, respectively.

30.1.5 Non-classical logics

Classical logic has severe limitations in its ability to handle real world situations. It deals with statements which are either true or untrue and does not accommodate information which is incomplete, vague, contradictory or unbelievable. It does not readily handle uncertainty and inconsistency.

It is a feature of classical logic that it is monotonic. The conclusions once derived are valid deductions and remain so. The set of facts and inferences can only increase; it cannot decrease. This does not accord well with real life, in which it is necessary to revise conclusions reached as more information becomes available.

Common-sense reasoning is therefore not well served by classical logic and there have been developed a number of non-classical logics which address particular deficiencies. Many of these deal with uncertainty and

inconsistency, but other aspects such as time are also accommodated.

These non-classical logics are considered in Section 30.7.

30.1.6 Probabilistic reasoning

Much knowledge relates in some way to uncertainty. The methods just described are not well adapted to representing knowledge under uncertainty, but other methods do exist for this purpose. Foremost among these are probabilistic reasoning and fuzzy logic.

Methods for handling uncertainty are described in Section 30.8 and those of probabilistic reasoning and fuzzy logic are described in Sections 30.9 and 30.10.

30.1.7 Structured knowledge

AI possesses a rich repertoire of methods for the storage of knowledge in structured forms. The creation of structure has a significance which goes far beyond simple ease of retrieval. It imposes a discipline which ensures that the entities and their relationships are formally defined and it facilitates basic operations such as search and matching.

Structured knowledge is considered in Section 30.12.

30.1.8 Graphs, trees and networks

A form of knowledge representation widely used by humans is diagrams in the form of graphs, trees and networks. There are a large number of such diagrams in common use and a number which have been developed in the course of AI work. These diagrams may be mapped into program structures and in many cases there are standard techniques available to do this. An outline of some of the graphs, trees and networks in use in AI is given in Section 30.22.

30.1.9 Programming languages

The programs of interest here are those which both contain representations of knowledge and perform operations on them. Such programs are most effectively implemented in programming languages of the declarative rather than the procedural type, the principal languages being LISP and Prolog. The strength of these languages is their ability to combine representation of knowledge in the forms required in AI work and support for various modes of reasoning. Programming languages are described in Section 30.11.

30.2 Databases

A widely used form of knowledge representation is the database. Databases are a major topic but may be treated here quite briefly.

Accounts of databases are given in *An Introduction to Database Systems* (Date, 1977), *Principles of Database Systems* (Ullman, 1982), and *The Theory of Relational Databases* (Maier, 1983). Data bases in the context of AI are discussed by Frost (1986) and Tanimoto (1990).

A database stores and provides ready access to data. It imposes a discipline on the classification and storage of data. It is a natural form for the storage of knowledge about certain types of relationship between data.

A rich variety of data structures are available, including: arrays, lists, strings, queues, stacks, bit maps and records; direct access, sequential, inverted and transposed files; hash tables; graphs and trees; and multi-lists, inverted lists and bit lists.

Aids to the design and implementation of data bases exist in the form of database management systems (DBMSs) which provide a collection of procedures, documentation aids, languages and programs.

Corruption of the database must be avoided and various formal systems are required. By controlling access a privacy subsystem protects against unauthorized alteration of the database. An integrity subsystem protects against invalid alteration by imposing a discipline on those authorized to make changes. A back-up and recovery subsystem provides a facility for rebuilding the database after corruption has occurred.

30.2.1 Relational databases

A form of database suited to the handling of large data sets with regular structure is the relational database. The term 'relation' is applied to a set of ordered n-tuples, or ordered sets each containing n items. An n-ary relation has n fields. The first field is referred to as the primary key. A field possesses a domain, which comprises the set of entities from which elements in the field may be drawn. A name is assigned both to the relation and to its fields.

The following table is an illustration of a 3-ary relation.

PIPE

Section	*Diameter* (in.)	*Material*	*Supplier*
Straight	3	Copper	X
Straight flanged	3	Mild steel	Y
90° bend	4	Stainless steel	Y
T-section	4	Stainless steel	Y

The relation is PIPE, the primary key is *Section*, the other fields being *Diameter*, *Material* and *Supplier*.

Some elementary operations which are supported by relational database programs include selection, projection and joining. Selection is the creation from an existing relation of a new, more specialized relation by selection of a subset of rows which have some common property. Projection is the creation from an existing relation of a new, more specialized relation by excision of some of the fields. Joining is the creation of a new relation by the fusion of two existing relations.

30.3 Propositional Logic

30.3.1 Propositions

Propositional logic deals with the relationships between propositions. Typical propositions are:

(1) The valve is open.
(2) The valve is open and the pipe is full of liquid.

The first of these is a simple proposition and the second a compound proposition. Propositions are also referred to as statements, sentences or formulas. Statements are represented by propositional symbols, which are capital letters, commonly P, Q, R, etc.

Table 30.2 *Some features of propositional logic*

A Connectives

Type	*Meaning symbol*	*Symbol*	*Alternative*
Negation	not	$\neg$	$\sim$
Conjunction	and	$\wedge$	&
Disjunction	or	$\vee$	$\vee$
Implication	if . . . then	$\Rightarrow$	$\rightarrow$
Double implication	if and only if	$\Leftrightarrow$	$\leftrightarrow$

B Some equivalence laws

Idempotency	$P \wedge P \equiv P$
	$P \vee P \equiv P$
Commutativity	$P \wedge Q \equiv Q \wedge P$
	$P \vee Q \equiv Q \vee P$
	$P \Leftrightarrow Q \equiv Q \Leftrightarrow P$
Associativity	$(P \wedge Q) \wedge R \equiv P \wedge (Q \wedge R)$
	$(P \vee Q) \vee R \equiv P \vee (Q \vee R)$
Absorption	$P \wedge (P \vee Q) \equiv P$
	$P \vee (P \wedge Q) \equiv P$
Distributivity	$P \wedge (Q \vee R) \equiv (P \wedge Q) \vee (P \wedge R)$
	$P \vee (Q \wedge R) \equiv (P \vee Q) \wedge (P \vee R)$
De Morgan	$\neg(P \wedge Q) \equiv \neg P \vee \neg Q$
	$\neg(P \vee Q) \equiv \neg P \wedge \neg Q$
Conditional elimination	$P \Rightarrow Q \equiv \neg P \vee Q$
Bi-conditional elimination	$P \Leftrightarrow Q \equiv (P \Rightarrow Q) \wedge (Q \Rightarrow P)$

C Truth table for equivalent statements

P	Q	$\neg P$	$P \wedge Q$	$P \vee Q$	$P \Rightarrow Q$
T	T	F	T	T	T
T	F	F	F	T	F
F	T	T	F	T	T
F	F	T	F	F	T

30.3.2 Syntax

The main feature of the syntax of propositional logic is the connectives, the symbols for which are shown in Table 30.2, Section A. Use is also made of parentheses ( ) as delimiters, but where there is no chance of ambiguity, parentheses may be omitted, in which case the order of precedence of the connectives is, from highest to lowest: $\neg$, $\wedge$, $\vee$, $\Rightarrow$, $\Leftrightarrow$.

The set of statements commonly used to illustrate the connectives is as follows:

$\neg P$
$P \wedge Q$
$P \vee Q$
$P \Rightarrow Q$
$P \Leftrightarrow Q$

30.3.3 Semantics

Some principal features of the semantics of propositional logic are the properties of statements and the rules of inference. The semantics of a statement is the truth value assigned to it, the process of assignment being known as interpretation.

The truth values assigned are true or false. These values are commonly denoted by T for true and F for false, particularly in truth tables. It should be noted that the symbols T and F themselves represent statements and are used in compound statements.

Some properties of statements are:

Satisfiability – a statement is satisfiable if there is an interpretation for which it is true.
Contradiction – a statement is contradictory, or unsatisfiable, if there is no interpretation for which it is true.
Validity – a statement is valid, or tautologous, if it is true for every interpretation.
Equivalence – two statements are equivalent if they have the same truth value for every interpretation.
Logical consequence – a statement is a logical consequence of another if it is satisfied by all interpretations which satisfy the first.

In the interpretation of compound statements use is often made of substitution of equivalent statements. Table 30.2, Section B shows some equivalence laws which may be used in making such substitutions. Another way of determining equivalence is the use of truth tables. A truth table for equivalent statements is shown in Table 30.2, Section C.

30.3.4 Inference rules

The means to perform deductions is provided by the rules of inference. Some principal rules are as follows.

Modus ponens

Assertion: P
Assertion: $P \Rightarrow Q$
Conclusion: Q

Chain rule

$P \Rightarrow Q$
$Q \Rightarrow R$
$P \Rightarrow R$

Disjunctive syllogism

P
$P \vee Q$

Resolution

$P \vee \neg Q$
$Q \vee R$
$P \vee R$

Other rules of inference are:

Substitution – if s is a valid statement, a statement s′ derived from it by consistent substitution is also valid.
Simplification – from $P \vee Q$ inference is P.
Conjunction – from P and Q inference is $P \vee Q$.
Transposition – from $P \Rightarrow Q$ inference is $\neg Q \Rightarrow \neg P$.

30.4 Predicate Logic

30.4.1 Basic entities

The basic entities handled in first order predicate logic (FOPL) are constants, variables, functions and predicates. The first three are referred to as terms, and predicates are referred to as atomic formulas, or atoms. An atom or its negation is referred to as a literal.

A constant is a term which has a fixed value and a variable is a term which can take different values. A function maps elements of the domain to further elements of the domain. A predicate maps elements of the domain to truth values. Commonly used constant symbols are *a, b, c*, . . . ; function symbols *f, g, h*, . . . ; variable symbols *x, y, z*; and predicate symbols P, Q, R . . . .

Use is also made of quantifiers. These are $\exists$ for existential quantification and $\forall$ for universal quantification. The meanings are:

$\exists x$ For some x; there is an x.
$\forall x$ For all x

The expression $\exists x \mathrm{P}(x)$ means that there exists at least one element of the domain which makes $\mathrm{P}(x)$ true.

30.4.2 Syntax

In respect of syntax, the logical connectives used in FOPL are the same as those for propositional logic.

30.4.3 Well-formed formulas

There are rules for the construction of syntactically correct formulas. Formulas derived by correct application of these rules are termed well-formed formulas, or wffs (pronounced woofs). An atomic formula is a wff. Wffs are obtained from predicates, or atomic formulas, by application of quantifiers and connectives.

Some wffs contain variables. If a variable follows or is within the scope of a quantifier, it is said to be bound; otherwise it is free. The variable x in the expression $\forall x(\mathrm{P}(x) \Rightarrow \mathrm{Q}(x, y))$ is bound, whereas the variable y is free. For a formula to be evaluated, it is necessary that all the variables in it be bound. This leads to the requirement that a wff should contain only bound variables.

A wff, or a predicate, which has no variable is referred to as a ground atom.

30.4.4 Semantics

The semantics of FOPL are somewhat more complex than those for propositional logic. They largely revolve around the conversion of wffs to clausal form and the application of the rules of inference and the principle of resolution.

Accounts of the semantics for FOPL, including equivalence and truth tables are given by Frost (1986) and Patterson (1990).

30.4.5 Clausal form

One of the most powerful methods of interpretation in FOPL is the resolution principle. But, in order to apply it, it is necessary first to convert the wffs to clausal form. A formal six-step procedure exists to effect this conversion.

30.4.6 Inference rules

Interpretation of the wffs is effected by application of the rules of inference for FOPL. One of these is modus ponens.

An illustration of modus ponens in FOPL is the following:

$$\begin{array}{ll} \text{Assertion} & \mathrm{P}(a) \\ \text{Implication} & \forall x\, \mathrm{P}(x) \Rightarrow \mathrm{Q}(x) \\ \hline \text{Conclusion} & \mathrm{Q}(a) \end{array}$$

In this interpretation since the implication $\mathrm{P}(x) \Rightarrow \mathrm{Q}(x)$ is true for all x, it is true in particular for $x = a$.

30.4.7 Resolution principle

Resolution is an inference procedure which is applied to a set of clauses to determine if the set is unsatisfiable.

The principle of resolution is as follows. If there are two clauses C1 and C2, the parent clauses, which have no variables in common and if there is a literal in C1 which is the complement of a literal in C2, both literals are deleted and a new clause C, the resolvent, is formed from the remaining reduced clauses.

An illustration of the principle is the following resolution:

$$\begin{array}{l} \neg \mathrm{P} \vee \mathrm{Q} \\ \neg \mathrm{Q} \vee \mathrm{R} \\ \hline \neg \mathrm{P} \vee \mathrm{R} \end{array}$$

There is a family of types of resolution applicable to particular combinations of numbers and of types of parent clauses.

30.5 Non-deductive Inference

The form of inference just described is deductive inference, but this is not the only form of inference in use. Other forms are abductive inference, inductive inference and analogical inference, and these are now described. These forms of inference are not strictly valid, but they are nevertheless in common use.

30.5.1 Abductive inference

Abductive inference may be represented as

$$\begin{array}{l} \mathrm{Q} \\ \mathrm{P}^{c} \Rightarrow \mathrm{Q} \\ \hline \mathrm{P} \end{array}$$

where the superscript c denotes a possible causal relationship. A proposition Q and a causal relation $\mathrm{P} \Rightarrow \mathrm{Q}$ are used to infer a proposition P.

30.5.2 Inductive inference

Induction involves generalization based on a limited sample of entities from the universe of entities. Inductive inference may be represented as:

$$\begin{array}{l} \mathrm{P}(a_1) \ldots \mathrm{P}(a_n) \\ \hline \forall x\, \mathrm{P}(x) \end{array}$$

30.5.3 Analogical inference

Analogical inference is based on the assumption that two situations which are similar in some respects are also similar in other respects. It in fact appears to utilize a combination of deductive, abductive and inductive inference. Analogical inference may be represented as:

$$\frac{P^r \Rightarrow Q}{P'^r \Rightarrow Q'}$$

where the superscript r means related to and superscript $'$ denotes similar to.

30.6 Production Rules

As already mentioned, one form in which knowledge may be represented is as a set of rules, also called productions. Such rules may be regarded as a special case of propositional logic.

The rules are of the type IF . . . THEN . . . . They have a left-hand side (LHS), which is variously known as the antecedent, premise, condition or situation and a right-hand side (RHS), which is known as the consequent, conclusion, action or response. The proposition on the LHS may be a compound one with a number of propositions ANDed together.

A suitable set of rules, or productions, can be used to form the basis of a production system. Production systems are one of the main methods of implementing expert systems and are discussed further below.

30.6.1 Production systems

A production system has three main features: the rule base, a working memory and the inference engine. The rule base holds the set of rules which embody the expertise of the system. The working memory is supplied with the input data, or facts, on the problem to which the rules are to be applied. The inference engine controls the operation of the rules to deduce conclusions from these data.

The rules in the rule base are laid out as a set of logic statements. The rule base may be inspected by an expert to check for correctness. Rules may be added, removed or modified with relative ease.

The operation of a production system is quite different from the execution of a program in a procedural language. Execution is not controlled by a procedure as such, but involves making a pass through the rule base and determining which rules are satisfied.

The inference engine applies the input facts to the rules and determines which rules are satisfied, or 'trigger'. Provided there is no conflict between the output from a rule and that for another rule, the rule then 'fires'.

30.6.2 Conflict resolution

If such conflict does occur, it becomes necessary to apply a suitable conflict resolution strategy. The application of this strategy determines which rules should fire.

The conflict resolution strategy used may be a generalized one or it may be one specific to the particular problem. There are a number of generalized strategies for conflict resolution. Winston (1984) lists the following six strategies: (1) specificity ordering; (2) rule ordering; (3) data ordering; (4) size ordering; (5) recency ordering; and (6) context limiting. Specificity ordering applies to a group of rules where the conditions of one rule are a superset of which the conditions in the other rules are subsets; priority is given to the rule with the superset of conditions. In rule ordering the rules are arranged in a priority list and rule first triggered has priority. In data ordering all possible aspects of the situation are arranged in a priority list and the rule having the highest priority condition has priority. In size ordering the rule has priority which has the largest number of conditions. In recency ordering priority is given either to the rule which fired most recently or, alternatively to that which fired least recently. Context limiting involves dividing the rules into groups and creating a procedure which activates and deactivates groups; those rules which are in the active groups, having priority.

30.7 Non-classical Logics

The point has already been made that a classical propositional logic is not sufficiently expressive. The creation of another, now classical, logic, the predicate calculus, was a response to this deficiency. The same need has given rise to the development of further, non-classical logics.

These newer logics extend the range of the knowledge which can be represented and are thus more expressive. They make it possible to handle knowledge which is incomplete, uncertain, vague and/or inconsistent, or associated with time. They are often more efficient in handling the knowledge.

The properties of a logic are that it has a well-defined method for representing knowledge, for obtaining proofs by syntactical manipulation and for extracting meaning using a semantic model.

30.7.1 Many-sorted logics

In a many-sorted logic the entities in the universe of discourse are divided into sorts. There are different sort structures. One is a structure where all the sorts are different, or disjoint. Another is a structure where the sorts are related as in a tree, with the sorts at a lower layer being subsets of those in the layer above. Another is a structure in which the sorts are related as in a lattice, with non-hierarchical links between them.

Such many-sorted logics are used to place appropriate limitations on searches, and thus to improve search efficiency, and on logical operations, and thus avoid nonsensical interpretations.

30.7.2 Situational logics

A situational logic is a method of representing relationships which pertain in a particular situation. The usual device for effecting this is to augment the predicate with an extra argument which denotes the situation.

30.7.3 Non-monotonic logic

The point was made earlier that the classical logics are monotonic logics. They do not accommodate the revisions which are necessary to cope with real-life situations. There are several reasons why it may become necessary to revise knowledge. One is that the original knowledge may have been incomplete so that a default

value had to be used. Another is that in problem-solving it is often necessary to make a temporary assumption. Another is that the situation may have changed.

30.7.4 Many-valued logics

The classical logics utilize in their semantics just two values, true and false. Other logics have been developed which permit the use of a wider range of values. One such many-valued logic is that of Lukasiewicz (1951), which utilizes three values. In addition to true and false, there is an intermediate value, which is applicable where the statement may be true, or 'sort of true'.

30.7.5 Fuzzy logic

Fuzzy logic, which is based on fuzzy sets, permits reasoning where there is uncertainty and vagueness. It is considered further in Section 30.10.

30.7.6 Modal logics

The classical logics deal with statements in the indicative mood concerning what is. There has been developed a family of modal logics which have been characterized as being in the subjunctive mood and which deal with what must be, should be, might be, is believed to be, etc.

Some principal modalities and the descriptor pairs associated with them are:

Alethic modality: necessary, possible.
Temporal modality: always, sometimes.
Deontic modality: obligatory, permissible.
Epistemic modality: known, believed.

Each modality has its associated modal operators. Thus for alethic modality operators are necessary (L) and possible (M).

30.7.7 Temporal logic

The classical logics do not accommodate time. The temporal logics which have been developed to overcome this limitation follow two broad approaches. One is the use of a temporal modality. In this form of temporal logic, use is made of the modalities:

Always, sometimes.

Other modalities used are:

Past, present, future

and

Precedes, succeeds.

There are corresponding temporal operators, of which the most common are probably always (A) and sometimes (S).

The other approach is to adapt FOPL to handle time. One method makes use of time points. The predicate is augmented with an extra argument which denotes the time point. The approach is somewhat similar to that used in situational logic.

30.7.8 Epistemic logic

Epistemic logic is a form of logic used to reason about knowledge possessed by other agents.

30.8 Uncertainty and Inconsistency

The foregoing discussion has brought out the need to be able to handle uncertainty and inconsistency. Some approaches to this problem are now described.

30.8.1 Sources of uncertainty

There are a number of sources of uncertainty. Uncertainty arises due to the randomness of events and to incompleteness, vagueness, unreliability, and unbelievability of and contradictions in knowledge.

30.8.2 Probability theory

The traditional approach to handling uncertainty is the use of probabilistic reasoning. This has been considered in some detail in Chapter 7. The treatment there was in the context of reliability engineering, but the basic probability theory is of wide applicability.

Probabilistic reasoning is utilized in AI and an account is given in Section 30.9. However, it also has a number of limitations, which have led to the development of alternative approaches. These limitations are perhaps best understood by considering these other techniques.

30.8.3 Certainty theory

Expert systems are typically based on a set of rules. In some cases it is not certain that a rule is correct. It is not easy to characterize this uncertainty using conventional probability theory and certainty theory has been developed to handle this problem.

For a statement S a certainty measure, or certainty, $C(\mathrm{S})$ is defined such that

$C(\mathrm{S})$	If S is true
$C(\mathrm{S}) = -1.0$	If S is false
$C(\mathrm{S}) = 0$	If nothing is known about S

$C(\mathrm{S})$ may also have values intermediate between $+1.0$ and -1.0, reflecting the degree of certainty that it is true or false.

For a rule a certainty factor CF is defined

If A then X with certainty factor CF

CF has the value 1.0 if it is certain that the rule is true, it has the value -1.0 if it is certain that the rule is false, and may take intermediate values, reflecting the degree of certainty that it is true or false.

In the approach, a rule is taken to be either true ($\mathrm{CF} = 1.0$) or false ($\mathrm{CF} = -1.0$), and its application results in a conclusion X which has a value true or false. A truth value of X is obtained by application of a single rule. Application of a second rule which gives a truth value for X either confirms the original value or contradicts it. Using certainty theory, however, the truth value of X is associated with a certainty value which is subject to adjustment each time a rule is applied and yields a truth value for X.

The relations used to determine the certainty $C(\mathrm{X})$ of the statement X given A are:

$$C(X|A) = C(X) + [\mathrm{CF}\ (1.0 - C(X))]\, C(X) > 0;\ CF > 0 \quad [30.8.1a]$$

$$C(X|A) = C(X) + [\mathrm{CF}\ (1.0 + C(X))]\, C(X) < 0;\ CF < 0 \quad [30.8.1b]$$

$$C(X|A) = \frac{C(X) + CF}{1.0 - min[|C(X)|;\ |CF|]} \quad C(X) > 0;\ CF < 0, \text{ or } C(X) < 0;\ CF > 0 \qquad [30.8.1c]$$

In the original work the certainty factor for a rule was formally related to the probability that it is true, as follows:

$$CF = \frac{max[P(X|A);\ P(X)] - P(X)}{1.0 - P(X)} \qquad CF > 0 \qquad [30.8.2a]$$

$$CF = \frac{min[P(X|A);\ P(X)] - P(X)}{P(X)} \qquad CF < 0 \qquad [30.8.2b]$$

The certainty factor CF in Equation 30.8.2a is also referred to as the measure of belief (MB) that the rule is true, and CF in Equation 30.8.2b as the measure of disbelief (MD).

In subsequent work certainty factors have often been used in a heuristic way to attach subjective estimates of certainty to rules. As an illustration of the application of certainty factors, consider the following illustrative example.

If A then X CF = 0.8
If B then X CF = 0.7

with an initial certainty $C(X) = 0$. For both rules the relation applicable is Equation 30.8.1a. Successive applications give for $C(X)$ values of 0.8 and 0.94.

30.8.4 Dempster/Shafer theory

The Dempster/Shafer theory is a theory of evidence which makes a distinction between uncertainty and ignorance. It utilizes a belief function which is essentially a probability function to which confidence limits have been assigned. In other words, the belief function gives the probability that the probability estimate lies within certain bounds.

As the bounds narrow, the belief function tends to the conventional probability function. In other words, probability theory may be regarded as a special case of Dempster/Shafer theory.

30.8.5 Possibility theory and fuzzy logic

Another type of uncertainty is that which arises from the vagueness of natural language. This can be handled using fuzzy logic. This approach is also known as possibility theory. Fuzzy logic is considered in Section 30.10.

30.8.6 Incidence calculus

In probability theory the relationships between events are based on the assumption that the events considered are independent. Formulations of the basic probability relations exist that incorporate correlation terms which allow for dependency between events. The problem is the difficulty of furnishing numerical values for these correlation terms.

An alternative approach is the use of the incidence calculus of Bundy (1984). A set W is defined which is the set of all possible worlds or incidents. The incidence $i(A)$ of a formula A with respect to W is that subset containing all those incidents for which A is true. The independence of two formulas is obtained from the intersection of the two incidences, or subsets.

30.8.7 Plausibility theory

Another problem which needs to be addressed is reasoning with knowledge obtained from sources which are not totally reliable. This is the province of plausibility theory. Plausibility theory makes it possible to reason with inconsistent sets of knowledge obtained from imperfect sources. It utilizes p-sets, a p-set being a set of assertions vouched for by sources with some degree of reliability. Each member of a p-set is assigned a plausibility value which is determined by reference to the source with the highest status.

30.8.8 Truth maintenance systems

As already described, non-monotonic reasoning involves revision, and therefore the possibility of introducing inconsistency into the knowledge base. It is the function of a truth maintenance system (TMS) to maintain the consistency of the knowledge base during the process of reasoning by the inference engine, which is thereby freed to get on with its main task. A TMS is also known as a belief revision system or revision maintenance system.

A TMS maintains a record of the current beliefs and of the justifications for these beliefs. It identifies contradictions and the statements responsible for them and implements retractions. The record of the knowledge base takes the form of a dependency network, the nodes of which represent premises, conclusions, rules, etc. Each node has attached to it a justification enumerating the inference steps by which it was derived. The exception is premise nodes, since premises require no justification.

Two types of justification record are used, support lists (SLs) and conceptual dependencies (CPs), the first being the more widely used. A support list takes the form

(SL <in-list> <out-list>)

An active node must have at least one valid node in the in-list and hence IN the current belief set, and all nodes in the out-list must be OUT of the belief set.

The state of a TMS may be represented in tabular form. A typical example might be:

Node	*Status*	*Support list*	
n1	IN	(SL ( ) ( ))	Premise
n2	OUT	(SL (n1) (n3))	Unjustified belief
n3	IN	(SL (n5) (n4))	Justified belief
n4	OUT	(SL ( ) ( ))	Retracted premise
n5	IN	(SL ( ) ( ))	Premise

The TMS can also be represented in graphical form using a special set of symbols.

When a contradiction is discovered, the TMS examines the dependency structure which supports the contradictory node and identifies the offending nodes directly. This process is termed dependency-directed backtracking (DDB) and is for this purpose a more efficient search strategy than chronological backtracking.

The other type of record, the conceptual dependency (CP), may be regarded as a form of conditional proof. It takes the form:

(CP <consequent> <hypothesis in-list> <hypothesis out-list>)

The CP is valid if the consequent node is IN when each node in the hypothesis in-list is IN and each node in the hypothesis out-list is OUT. CPs can be, and usually are, converted to SLs.

There are a number of different types of TMS. These include the non-monotonic TMS (NMTMS) or justification-based TMS (JTMS); the logic-based TMS (LTMS); and the assumption-based TMS (ATMS).

30.8.9 Default reasoning

Another form of non-monotonic logic is default reasoning. This permits default assumptions to be handled. The method is non-monotonic because it may be necessary at some later stage to retract an assumption.

Default reasoning may be represented as

$$\frac{\mathrm{P}(x):\ \mathrm{MQ}(x)}{\mathrm{R}(x)}$$

where M is a consistency operator, which has the meaning 'and if it is consistent to assume...'.

30.8.10 Default reasoning: closed world assumption

The method of default reasoning just described is suitable for making specific individual default assumptions, but it is sometimes desirable to be able to make some more global set of assumptions. This is the function of the closed world assumption (CWA).

The closed world assumption is that if a proposition cannot be proven it is false. It is often a reasonable assumption in a situation which is well understood and in which most of the facts are known.

Formally, the CWA involves the use of a metarule that if $\mathrm{P}(a)$ cannot be disproved, the assumption $\neg\mathrm{P}(a)$ is to be made.

30.8.11 Default reasoning: predicate completion and circumspection

Whilst default assumptions are valuable, they need to be carefully handled. Proliferation of default assumptions can cause problems. Two methods of doing this are predicate completion and circumspection.

Predicate completion involves the use of completion formulas to restrict the application of predicates to those entities to which they are applicable.

Circumspection formulas fulfil a somewhat similar function by restricting the entities to which a predicate is applied to those with defined characteristics.

30.8.12 Heuristics

In many AI applications, particularly in expert systems, use has been made of heuristics and of *ad hoc* methods to take account of uncertainty. There are no doubt various reasons for this. One is probably unfamiliarity with the more formal methods available. Another is the difficulty of providing the probability estimates required in many formal methods.

A feature for which heuristics have been developed is the treatment of the degree of confidence in particular rules. For example, the expert system SOLOMON of P.R. Cohen (1985) utilizes a system of 'endorsements', effectively weightings, to be applied to rules.

30.9 Probabilistic Reasoning

30.9.1 Probability

Probability theory is considered at some length in Chapter 7 and it is sufficient here to restate the following basic relations for independent events A and B:

$$P(\mathrm{A\ AND\ B}) = P(\mathrm{A})^{*}P(\mathrm{B}) \qquad [30.9.1]$$

$$P(\mathrm{A\ OR\ B}) = P(\mathrm{A}) + P(\mathrm{B}) - P(\mathrm{A})^{*}P(\mathrm{B}) \qquad [30.9.2]$$

$$\neg P(\mathrm{A}) = 1 - P(\mathrm{A}) \qquad [30.9.3]$$

30.9.2 Bayes' rule

Much use is made in AI of Bayesian inference. Restating Bayes' rule for an event E and a hypothesis H

$$P(\mathrm{H}|\mathrm{E}) = \frac{P(\mathrm{E}|\mathrm{H})^{*}P(\mathrm{H})}{P(\mathrm{E})} \qquad [30.9.4]$$

Generalizing for a set of hypotheses $\mathrm{H}_1 \ldots \mathrm{H}_n$:

$$P(\mathrm{H_i}|\mathrm{E}) = \frac{P(\mathrm{E}|\mathrm{H}_i)^{*}P(\mathrm{H}_i)}{\sum_1^n P(\mathrm{E}|\mathrm{H}_j)P(\mathrm{H}_j)} \qquad [30.9.5]$$

30.9.3 Odds

Another formulation of probability which is often used in AI is odds. The odds $O(\mathrm{E})$ in favour of an event E are related to its probability $P(\mathrm{E})$ as follows:

$$O(\mathrm{E}) = \frac{P(\mathrm{E})}{1 - P(\mathrm{E})} \qquad [30.9.6]$$

or, alternatively,

$$P(\mathrm{E}) = \frac{O(\mathrm{E})}{1 + O(\mathrm{E})} \qquad [30.9.7]$$

For Bayes' rule, where there is a hypothesis H, the two associated ratios of likelihood are

$$\mathrm{LS} = \frac{P(\mathrm{E}|\mathrm{H})}{P(\mathrm{E}|\neg\mathrm{H})} \qquad [30.9.8]$$

$$\mathrm{LN} = \frac{P(\neg\mathrm{E}|\mathrm{H})}{P(\neg\mathrm{E}|\neg\mathrm{H})} \qquad [30.9.9]$$

These relationships are used, for example, in the expert system PROSPECTOR. In the terminology there used the two likelihood ratios are termed logical sufficiency (LS) and logical necessity (LN).

Another useful concept associated with odds is that of the weight of evidence. In the use of Equation 30.9.4, the process of updating for a series of events $E_1 \ldots E_n$ is somewhat clumsy. An elegant device introduced by Turing is to reformulate using odds and then to take logarithms. This gives

$$\log_{\mathrm{e}} O(\mathrm{H}|\mathrm{E}) = \log_{\mathrm{e}} O(\mathrm{H}) + \sum_{i=1}^{n} w_i \qquad [30.9.10]$$

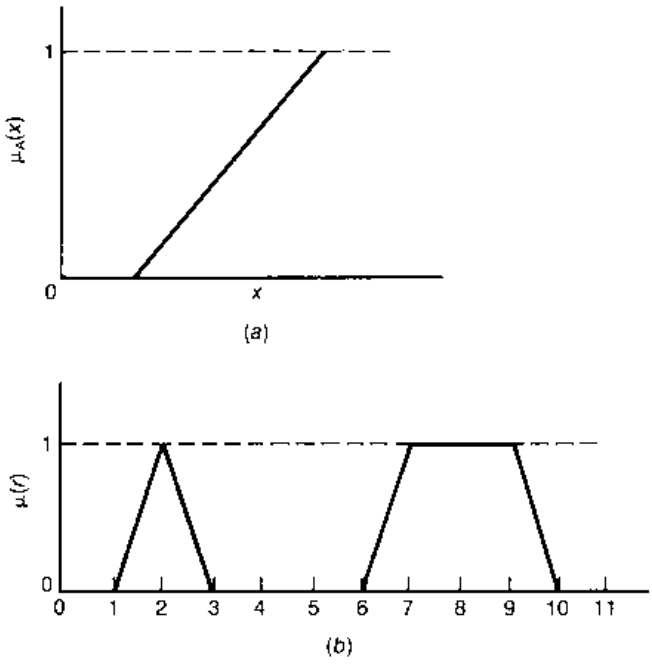


Figure 30.1 *Some functions in fuzzy logic: (a) membership function of a fuzzy set (b) two examples of a fuzzy number*

with

$$w_i = \log_e\left(\frac{P(E_i|H)}{P(E_i|\neg H)}\right) \quad [30.9.11]$$

$$= \log_e f_i \quad [30.9.12]$$

where f_i was termed by Turing the Bayesian factor in favour of H yielded by E_i, and w_i is the weight of evidence.

30.10 Fuzzy Logic

Fuzzy logic, and fuzzy set theory generally, addresses the problem of vagueness as opposed to randomness. The term fuzzy logic is used in two senses. In the broader sense it is virtually co-terminous with fuzzy set theory, whilst in the narrower sense it refers to that part of fuzzy set theory which deals with inference.

Fuzzy set theory was introduced by Zadeh (1965). Accounts are given in *Fuzzy Sets and Systems* (Dubois and Prade, 1980), *Multistage Decision-Making under Fuzziness* (Kacprzyk, 1983), *Fuzzy Sets Theory and Its Applications* (Zimmerman, 1986), *Fuzzy Sets, Decision-Making and Expert Systems* (Zimmerman, 1987), *Fuzzy Relation Equations and Their Application to Knowledge Engineering* (di Nola *et al.*, 1989) and *Fuzzy Logic for the Management of Uncertainty* (Zadeh and Kacprzyk, 1992) and by Zadeh (1968, 1975a,b, 1978, 1983a,b, 1985) and Kacprzyk (1992).

Fuzzy logic provides a means of handling the vagueness inherent in natural language. Some of the quantities with which it deals are:

Fuzzy predicates: *small, large; young, old*
Predicate modifiers: *very, quite, extremely*
Fuzzy quantifiers: *most, many, few, often, usually*
Fuzzy numbers: *about* n, *a little more than* n
Fuzzy probabilities: *likely, unlikely*
Fuzzy possibilities: *quite possible, virtually impossible*
Fuzzy truth values: *true, quite true, mostly untrue*

Fuzzy quantifiers are also termed linguistic quantifiers, and predicate modifiers are also termed linguistic hedges.

Fuzzy logic effectively involves a numerical encoding of natural language terms, or linguistic variables. It is sometimes known as linguistic variable theory.

If $X = \{x\}$ is a universe of discourse, consider a fuzzy set A which is a subset of X, denoted $A \subseteq X$. The set A is a set of ordered pairs $\{(x_A, \mu_A(x))\}$. Then $\mu_A(x)$ is the grade of membership of x in A.

For example if X = {1, 2, . . . , 10}, a fuzzy set for large numbers might be given as A = 0.3/6 + 0.5/7 + 0.85/8 + 1/9 + 1/10, where the grade of membership of the numbers 1–5 is zero, where that of the number 6 is 0.3, meaning that there is a probability of 0.3 that 6 is a member of the set, and so on.

The grade of membership in a set may be defined in terms of a membership function. Figure 30.1 shows two functions commonly used. Figure 30.1(a) is a form used for a linguistic variable such as a fuzzy quantifier and Figure 30.1(b) is a form used for a fuzzy number.

For the determination of the number of members in a fuzzy set with a given attribute, if A is the set of n items and $x_1, \ldots x_n$ the members of that set and these

members have to some degree the attribute F and therefore have a membership function $\mu_F(x_i)$, the number n_F of items which have this attribute F, or cardinality of the set, is determined as

$$n_F = \sum_{i=1}^{n} \mu_F(x_i) \qquad [30.10.1]$$

As an illustration, consider the problem of a set of items some of which are said to need replacement. If this set is $A = 0.3/x_1 + 0.3/x_2 + 0.8/x_3 + 0.8/x_4 + 0.8/x_5$, then from Equation 30.10.1 $n_F = 3.0$.

For the determination of the truth of a statement involving a fuzzy quantifier, such as 'most x's are F', the problem may be posed as the evaluation of the truth value τ of the statement, which may be expressed in a form such as $\tau(Qx\text{'s are F})$, where $A = \{x_1 \ldots x_n\}$ is the set of interest, F is an attribute and Q is a fuzzy quantifier. The grade of membership of an item x_i in the set A with respect to the attribute F is $\mu_F(x_i)$. The membership function is $\mu_Q(r)$. Then the relations for the determination of the truth value are

$$r = \frac{1}{n}\sum_{i=1}^{n} \mu_F(x_i) \qquad [30.10.2]$$

$$\tau(Qx\text{'s are F}) = \mu_Q(r) \qquad [30.10.3]$$

As an illustration, consider the problem of determining the truth of the statement 'Most compressors are reliable'. The problem is then to evaluate the truth value τ of this statement which may be expressed as $\tau(Qx\text{'s are F})$, where A is the set of n compressors, F is the attribute *reliable* and Q is the fuzzy quantifier *most*. Suppose that the grades of membership $\mu_F(x_i)$ for the attribute *reliable* in the set of compressors are taken as $A = 0.1/x_1 + 0.6/x_2 + 0.8/x_3$ and that the fuzzy quantifier may be represented by a suitable membership function $\mu_Q(r)$ taken as

$$\begin{aligned} &\mu_Q(r) = 1 && r \geq 0.8 \\ &\mu_Q(r) = 2r - 0.6 && 0.3 < r < 0.8 \\ &\mu_Q(r) = 0 && r \leq 0.3 \end{aligned}$$

Then from Equations 30.10.2 and 30.10.3 $r = 0.5$ and $\mu_Q(r) = 0.4$, giving a truth value τ of 0.4 also.

For fuzzy logic there is no unique set of inference rules, but the following are those most generally quoted. In terms of the truth value τ

$$\begin{aligned} &\tau(\neg A = 1 - \tau(A) && \text{Negation} \\ &\tau(A \wedge B) = \min(\tau(A),\ \tau(B)) && \text{Conjunction} \\ &\tau(A \vee B) = \max(\tau(A),\ \tau(B)) && \text{Disjunction} \end{aligned}$$

The application of inference rules in fuzzy logic tends to be considerably more complex than the corresponding exercise in classical logics.

30.11 Programming Languages

Many accounts of knowledge representation and of inferential reasoning give examples cast either in the form of the predicate calculus or of a specific programming language such as LISP or PROLOG. This section is a short introduction to these three languages, which is given for the purpose of making more concrete some of the concepts in the preceding sections and indicating how they are implemented in practice.

30.11.1 Predicate calculus

Knowledge representation and inferential reasoning are often exemplified using not a specific programming language but the predicate calculus. This is the approach adopted, for example, by Charniak and McDermott (1985).

The following are examples of some of the forms of knowledge representation and of inferential reasoning described in earlier sections cast in predicate calculus form.

Assertions

(inst vessel-1 vessel)	Vessel-1 is an instance of a vessel.
(structure vessel-1 thick-walled)	A structural feature of vessel-1 is that it is thick-walled.
(opens fitter flange)	A fitter opens a flange.

Isa hierarchy

(isa pump pressure-raiser)	A pump is a pressure raiser.

Connectives

(if (and (inst thermocouple instrument) (robustness instrument delicate) (robustness thermocouple delicate)	If a thermocouple is an instrument and an instrument is delicate then a thermocouple is delicate.

Quantifiers

(forall x (if (inst x instrument) (robustness x delicate)	All instruments are delicate.
(forall x (if (control-valve x) (exists y) (power-source-of x y)	All control valves have a power source.

1.	(inst thermocouple instrument)	A thermocouple is an instrument.
2.	(forall x (if (inst x instrument) (robustness x delicate)	All instruments are delicate.
3.	(if (inst thermocouple instrument) (robustness thermocouple delicate)	If a thermocouple is an instrument, then a thermocouple is delicate.
4.	(robustness thermocouple delicate)	A thermocouple is delicate.

The third entry is obtained from universal instantiation and assertion 2 and the fourth by modus ponens from assertions 3 and 1.

Abductive inference

(has-inspections vessel-1)	Vessel-1 has inspections.

(for all *x* (if (contains-chlorine *x*) (has-inspection *x*))	All vessels which contain chlorine have inspections.
(contains-chlorine vessel-1)	Vessel-1 contains chlorine.

This example illustrates the fact that abductive inference is not a strictly valid form of reasoning and may given a incorrect conclusion.

Inductive inference

(if (inst instrument-1 instrument) (robustness instrument-1 delicate)	Instrument-1 is delicate.
(if (inst instrument-2 instrument) (robustness instrument-2 delicate)	Instrument-2 is delicate.
(forall *x* (if (inst *x* instrument) (robustness *x* delicate)	All instruments are delicate.

Frame
An assertion

(opens fitter flange)	A fitter opens a flange.

may be cast in the frame form as

(opens opens-1)	Opens-1 is an instance of opening.
(agent-opening opens-1 fitter)	The agent opening is a fitter.
(object-opened opens-1 flange)	The object opened is a flange.

Forward chaining

(if (inst ?*x* pump) (inst ?*x* pressure-raiser)	If an object is a pump, then it is a pressure-raiser.

30.11.2 LISP

LISP (List Processing language) is a high level, symbolic processing language devised by McCarthy (1960, 1978) and embodies his calculus for symbolic processing.

Accounts of LISP are given in *LISP 1.5 Primer* (Weissman, 1967), *The Little LISPer* (D.P. Friedman, 1974), *Let's Talk LISP* (Siklossy, 1976), *Anatomy of LISP* (J. Allen, 1978), *A Beginner's Guide to LISP* (Hasemer, 1984a), *Common LISP* (Steel, 1984), *LISP* (Winston and Horn, 1981) and by D. Shaw, Swartout and Green (1975), J. Allen (1979), Pratt (1979), Hasemer (1984b), Laubsch (1984), Patterson (1990), Tanimoto (1990) and Gabriel (1992).

LISP can be run in the interpreted or compiled modes, the former being more commonly used.

There are a number of dialects of LISP. A widely used form is Common LISP, which was created in an attempt to obtain a standard form. There are, however, several other widely used forms, including MACLSP and INTERLISP.

The syntax of LISP is very simple. All data and program statements are represented in LISP as s-expressions. The valid s-expressions are the following: atoms, strings, lists and dotted pairs. An atom is a number or string of contiguous characters, including letters, numbers and special characters. A string is a sequence of characters enclosed in double quotation marks. A dotted pair, or cons, is an ordered pair of s-expressions enclosed in parentheses. A list is a sequence of s-expressions enclosed in parentheses.

Atom	a–b
String	"a b"
Dotted pair	(a · b)
List	(a b)

The basic operation of LISP is evaluation.

Instruction in LISP are described as forms. There are three basic types: functions, macros and special forms.

LISP contains a number of forms, which include the following: input and output forms; control forms; list manipulation forms; arithmetic functions; logical functions; evaluation forms; predicates; and function and property forms.

A principal feature of LISP is list processing and it possesses a number of functions for the manipulation of lists. These include cons, car, cdr, and append.

30.11.3 Prolog

Prolog (Programming in Logic) is a programming language based on the predicate calculus. A number of researchers contributed to its origins; it was implemented by Colmerauer and co-workers (Colmerauer, Kanoul and van Caneghem, 1983).

Accounts of Prolog are given in *Programming in Prolog* (Clocksin and Mellish, 1981), *The Art of Prolog* (Sterling and Shapiro, 1986) and *Prolog Programming for Artificial Intelligence* (Bratko, 1986) and by K.L. Clark and McCabe (1982), Clocksin (1984), J. Cohen (1985), Colmerauer (1985) and Patterson (1990).

Programming in a language such as Prolog is referred to as logic programming. Prolog programming may be viewed as the creation of a database of facts and rules about objects, their attributes and relationships. This database can then be interrogated.

Prolog has a simple syntax. A program consists of *terms*. A term is a *constant*, a *variable* or a *structure*. It consists of a sequence of *characters*. A character may be of four kinds: an upper case letter, a lower case letter, a digit or an operator. A constant may be of two kinds: an *atom* or an *integer*. Examples of atoms are:

vessel
pressure_raiser

A variable is similar to an atom except that it starts with an upper case letter of underline sign '_'. A structure consists of a *functor* and of *components*, with the functor written first followed by the components in parentheses. An example of a structure is:

pressure_raiser(pump)
meaning 'a pump is a pressure raiser'.

Facts
A fact or assertion is exemplified by:

corrodes(wet_chlorine, mild_steel)
meaning 'wet chlorine corrodes mild steel'

Rules
A rule is cast in the form:

conclusion if condition 1 and condition 2 . . .

where the first term is the head and the rest is the body. Such a form is termed a Horn clause. An example of a rule is

corrodes(X, Y): wet_chlorine(X), mild_steel(Y)

where : denotes *if* and the commas between the structures *and*. The meaning is X corrodes Y if X is wet chlorine and Y is mild steel.

Lists
A list is written as a sequence of terms with commas between and enclosed in square brackets. An example of a list is:

[steel, aluminium, copper]

An empty list is denoted by [ ].

The head and tail of a list may be distinguished by the use of a vertical bar. An example of this is:

[a|b, c, d]

List manipulation
There are a number of list manipulation functions: append, member, conc, add, delete; conc denotes concatenate.

Queries
A query is exemplified by:

?-corrodes (X, mild_steel)
meaning 'what X corrodes mild steel?'.

Prolog program
A Prolog program proceeds by taking the rule condition, or headless Horn clause, and 'instantiating' the variables (X and Y in the above examples) to identify those instances which satisfy the rule. Thus for the rule given above the clause

?- wet_chlorine (X), mild_steel(Y)

satisfies

corrodes(X,Y)

The program continues by this process of resolution. A Prolog program may be regarded as a resolution theorem prover for Horn clauses.

The search strategy used in Prolog is depth-first. This strategy is in many ways simpler, but it does involve backtracking and the search can get into a 'loop'.

30.11.4 Object oriented programming

Another type of language which is now widely used in AI is object oriented programming (OOP).

Object oriented programming is described in *SMALLTALK-80, The Language and its Implementation* (Goldberg and Robsen, 1983) and in *Object Oriented Programming* (B.J. Cox, 1986) and by Stephanopoulos (1987) and Hodgson (1991).

In object oriented programming, the program consists entirely of objects. An object is a frame-like entity with slots which hold not only data but also procedures. Procedures may perform a wide range of functions such as symbolic manipulation, numerical calculation and inferencing. Objects are arranged in hierarchies. Computation involves the sending of messages between objects.

One feature of object oriented programming is data encapsulation. Data structures incorporate within themselves the procedures which are used to manipulate them. An object can be regarded as a frame with slots which are the operations allowable on the object.

Another feature is the class hierarchy. At the top of the hierarchy is a single-object class, consisting of the principal object. Other objects lower down in the hierarchy belong to classes which are in effect subclasses. Inheritance occurs through the hierarchy.

Object oriented programming is an extremely powerful tool. A whole manufacturing process may be represented as an object, covering not only the physical plant but also its operation, documentation, hazards, and so on.

30.11.5 C++ programming language

Of the more conventional programming languages, mention should be made in particular of C++. This language supports object oriented programming and interfaces with both LISP and Prolog.

30.11.6 Language characteristics and facilities

Work in AI makes use of a number of languages, and there are major differences between them. An account is given by Frost (1986). A distinction is often made between procedural languages and declarative languages, with conventional languages such as FORTRAN being described as procedural and those such as LISP and Prolog as declarative. However, the term procedural is not well defined.

The essential distinction is whether or not the 'flow of control' is specified. The flow of control is specified in conventional languages, using such commands as GO TO statements and DO loops, but not in languages such as LISP and Prolog. In these latter declarative languages there are no explicit commands which determine the flow of control. This does not mean, however, that the programmer has no influence on control. In a language such as Prolog the flow of control is affected by the order in which the statements are written.

Languages used in AI work include: the functional language LISP; the logic programming language Prolog; the frame languages AM and KRL; and the script language SAM.

The flexibility of a language may be increased by the use of an add-on facility. Thus, for example, the program FLEX provides Prolog with an object oriented enhancement.

A language such as Prolog is used particularly as a research tool. A commercial implementation may well be rewritten in a conventional language such as C++.

30.12 Structured Knowledge

The foregoing sections have described some ways of representing knowledge. It is now necessary to consider

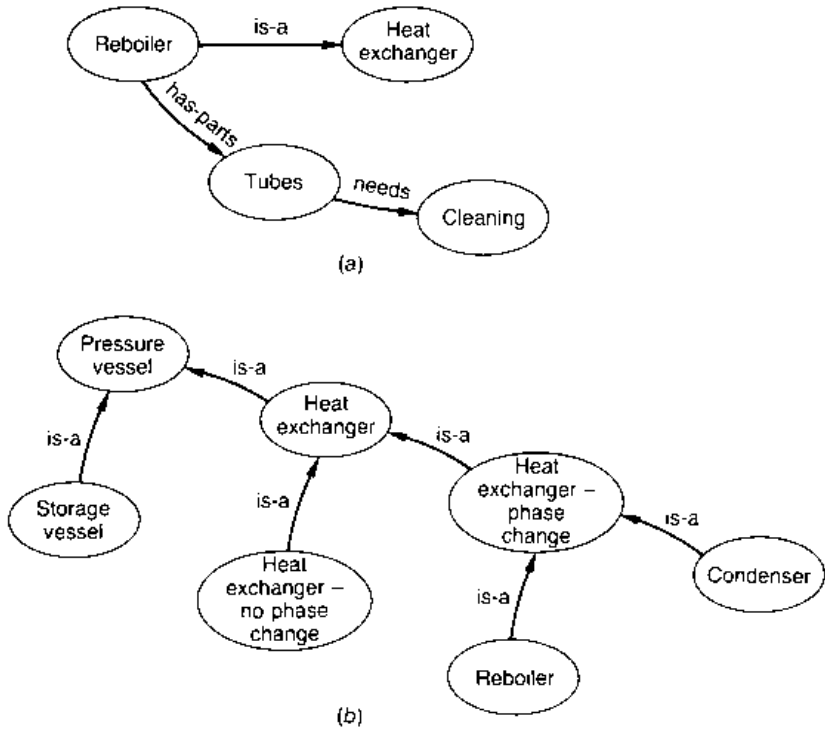


Figure 30.2 *(a) An associative network and (b) an isa network*

in more detail the representation of knowledge in structured form.

30.12.1 Indexing

A basic form of structure is that provided by the use of indexing, addresses, pointers and lists. These structures are not, however, generally sufficient for the purposes of AI.

30.12.2 Associative networks

A widely used form of representation in AI is the associative network. This is a form of directed graph with labelled nodes and arcs. An example is shown in Figure 30.2(a). An associative network may be expressed in terms of the predicate calculus, with nodes and arcs represented by terms and relations. An example illustrating this equivalence for a blocks world scene is given by Charniak and McDermott (1985).

The arcs of an associative network may represent a number of different relations. Some principal relations are:

Label	*Meaning*	*Used with*
is-a	Is an instance of	Generic noun
has	Has as parts	Specific noun
ako	Is a kind of	Generic noun
is	Is	Attribute
member-of	Is a member of	Larger set or entity
subset-of	Is a subset of	Larger set or entity

The ISA and HAS links are of particular importance for inheritance.

30.12.3 ISA hierarchy

A particular aspect of associative nets is the ISA hierarchy. This is effectively a way of expressing a taxonomy using a network with is-a arcs and working down from the generic to the specific. The associative network is shown in Figure 30.2(b) is an example of an ISA hierarchy.

30.12.4 Inheritance

Children can inherit a characteristic from their parents. Similarly, entities in an ISA hierarchy may inherit from entities directly above them. Another way of putting this is that a set can inherit a characteristic from a superset of which it is part, and a subset can inherit from a set. Multiple inheritance occurs when a set is part of more than one superset and may thus inherit from both supersets. This obviously creates the potential for conflict between the inherited values.

As stated earlier, the use of inheritance may be regarded as a form of default reasoning. The point has also been made, however, that the proliferation of defaults through inheritance can cause problems and it is necessary to proceed cautiously. In some cases it may be appropriate to allow most members of a set to inherit a certain characteristic but to arrange to override this for some members of the set.

30.12.5 Semantic networks

Associative networks are widely used in natural language comprehension and are then often termed semantic networks

30.12.6 Slot and filler systems

Another type of representation goes by the general name of a slot and filler system. Particular forms are frames and scripts. In terms of the predicate calculus, a slot and filler system may be represented by a single statement with a number of arguments corresponding to the number of slots.

Slot and filler systems are useful for: representing archetypes, or stereotypes; handling default values; matching and pattern recognition; and error detection.

30.12.7 Conceptual dependency

Before considering particular slot and filler systems, it is appropriate to mention conceptual dependency (CD) theory. The basic concept here is that a set of sentences which have different structures but identical meaning should have a CD representation which is both unique and unambiguous. CD methodology provides a set of tools such as primitives, syntax, rules, etc., for the formulation of such sentences.

30.12.8 Frames

A frame is a structure which contains a number of pieces of information on some entity such as an object, event or situation. It is applicable where the entity has a stereotype that is sufficiently strong to define the features on which information should be stored. Typical situations treated in the AI literature are attending a meeting or eating in a restaurant.

A frame consists of a frame name and a list of attribute–value, or slot–filler, pairs. In other words, the attributes are also called slots and the values fillers. A slot is simply the name of an attribute and the filler its value. Many accounts use the mixed terminology of slots and values, and this is adopted here. An empty frame, or schema, contains only the frame and slot names, whilst an instantiated frame contains also the values. In some cases default values may be supplied for slots.

Alternatively, or in addition, a slot may be furnished with associated information in the form of a procedural attachment, or demon. Two commonly used types of attached information are a procedure to determine the value for the slot if one is needed (the if-needed attachment) and one to be executed when the value has been filled in (the if-added attachment). Another type is a constraint on the value which can be added to the slot. A slot may also be filled with the name of another frame. In this way hierarchies of frames may be created.

Frames are a natural form of representation for default reasoning and for inheritance.

30.12.9 Scripts

Like a frame, a script is a structure which contains a number of pieces of information on some entity such as an event, situation or activity. It differs in that the slots contain not values but sentences written in terms of CD primitives. Typical situations treated in the AI literature are eating in a restaurant or shopping in a supermarket.

Thus a script will typically have a script name and slots for the situation, actors, initial conditions and props. There will then be slots for several scenes and one for the outcomes.

A script may be used to reason about a current situation by filling in those parts which characterize the situation, retrieving from memory another script which matches this situation. Slots in the current script are filled by inference using inherited and default values.

Like frames, scripts are a natural form to use for default reasoning and inheritance.

30.12.10 Constraints

A simple constraint may be represented as a predicate of the predicate calculus. Alternatively, it may be required to represent a more generalized constraint in the form of an algebraic equation relating several variables. In this case a constraint schema may be created which lists the variables in the equation and, for each of these variables, the algebraic expression by which it is evaluated.

30.12.11 Relational databases

Another form of structured knowledge representation is the relational database. This has been described in Section 30.2.

30.12.12 Production systems

Another form of structured knowledge is a production system. Production systems have already been described in Section 30.6 and are therefore not considered further here, except to note that the knowledge held in a production system is not necessarily confined to that embodied in the rules, but may include, in the conflict resolution section, knowledge about the control strategy which governs the application of the rules. It is often in this latter that much of the expertise resides.

30.12.13 Objects

Objects constitute another form for the representation of structured knowledge. They have been described in the previous section in the context of object oriented programming.

30.13 Search

The application of the tools described to problem-solving typically involves some form of search. Search is one of the fundamental activities in AI.

30.13.1 Search procedures

There are a large number of search procedures which are used in AI. They may be classified in several ways.

Some procedures are used to search for optimal paths; others for any path, not necessarily an optimal one; and others again for game playing. Another distinction is between uninformed, unguided, or blind search and informed or guided search. Some principal procedures category are:

General	*Informed*	*Optimal*
Breadth-first	No	No[a]
Depth-first	No	No[a]
Hill-climbing	Yes	No
Beam	Yes	No
Best-first	Yes	No
British Museum	No	Yes
Branch and bound	Yes	Yes
A* algorithm	Yes	Yes
Games		
Minimax		
Alpha beta		

[a] Search does not necessarily find the optimal, or shortest, path unless it is exhaustive.

30.13.2 Uninformed search
Uninformed search is inefficient, but it may be necessary to resort to it if there is difficulty in formulating heuristics or an evaluation function to guide the search.

30.13.3 Breadth-first search
Breadth-first search involves visiting all the nodes at a given level before moving to the next level. A breadth-first search is illustrated in Figure 30.3(a).

30.13.4 Depth-first search
Depth-first search involves moving down the tree as rapidly as possible, visiting nodes at successively lower levels until the lowest node in the branch is reached, then returning back up the tree to the point at which a downward move again becomes possible, and so on. A depth-first search is illustrated in Figure 30.3(b). A depth-first search, therefore, necessarily involves backtracking.

30.13.5 Informed search
It will be clear from the account just given that uninformed search methods are subject to combinatorial explosion and become impractical for larger problems. The remedy is to inform the search in some way.

30.13.6 Heuristic search
One approach to informed search is the use of heuristics. These may take various forms, but generally have to do with the characteristics of the goals, states and paths between states.

30.13.7 Evaluation function
It may be possible to guide the search by using a formal evaluation function, which may also go by other names such as an objective function or a figure of merit. The formulation of such a function is an aspect of matching, which is discussed in Section 30.14. Given an evaluation function it becomes possible to utilize search methods which are much more efficient. The sum of the values of an evaluation function between the nodes on a path is known as the path length.

30.13.8 Hill-climbing
A hill-climbing search utilizes an evaluation function which it seeks to minimize and is essentially a form of depth-first search. It differs from a regular depth-first search in that at a given node the next move made is to the child node for which the evaluation function is minimized. A hill-climbing search is illustrated in Figure 30.3(c).

Like other forms of hill-climbing, there are certain classic topological problems which a hill-climbing search may encounter. They include the foothill, plateau and ridge problems.

Although, in general, hill-climbing is a common form of optimization, a hill-climbing search as just described does not guarantee a global optimum solution.

30.13.9 Beam search
A beam search resembles a breadth-first search in that it proceeds level by level, but differs from it in that the search utilizes an evaluation function and moves downwards only through the best w nodes at each level. A beam search is illustrated in Figure 30.3(d). By comparison with breadth-first search, beam search is much more economical.

30.13.10 Best-first search
A best-first search resembles hill-climbing in that it utilizes an evaluation function, but differs from it in that it uses this function in a different way. Whereas in hill-climbing the function is used to select between the child nodes of the current node, in a best-first search the function values for all nodes visited are stored and the search moves from the node for which the function is a minimum, wherever it may be in the tree. A best-first search is illustrated in Figure 30.3(e). Like hill-climbing, a best-first search does not guarantee a global optimum.

30.13.11 British Museum method
Of the methods which provide an optimum solution, the British Museum method involves an exhaustive search through the whole tree to identify the optimum path. The search may be breadth-first or depth-first, but in either case it is modified so that it does not stop when a path is found but continues until all paths are found and the optimum can be identified. The method is even more subject to combinatorial explosion than the regular uninformed search methods.

30.13.12 Branch-and-bound search
A branch-and-bound search proceeds by storing the path lengths and expanding that node which at any given stage has the shortest path length. This means that the search may move down a path in one branch of the tree and then jump to one in a second, quite different, part of the tree when movement down the current path has raised the path length above that in the second part. A branch-and-bound search is somewhat complex; an account is given by Winston (1984).

In this search method termination when a path is found does not actually guarantee an optimal solution, since in principle there may be a path which is incomplete but very close to the solution point. For an optimal solution, it is necessary to use the condition that termination occurs when the shortest complete path is shorter than the shortest incomplete one.

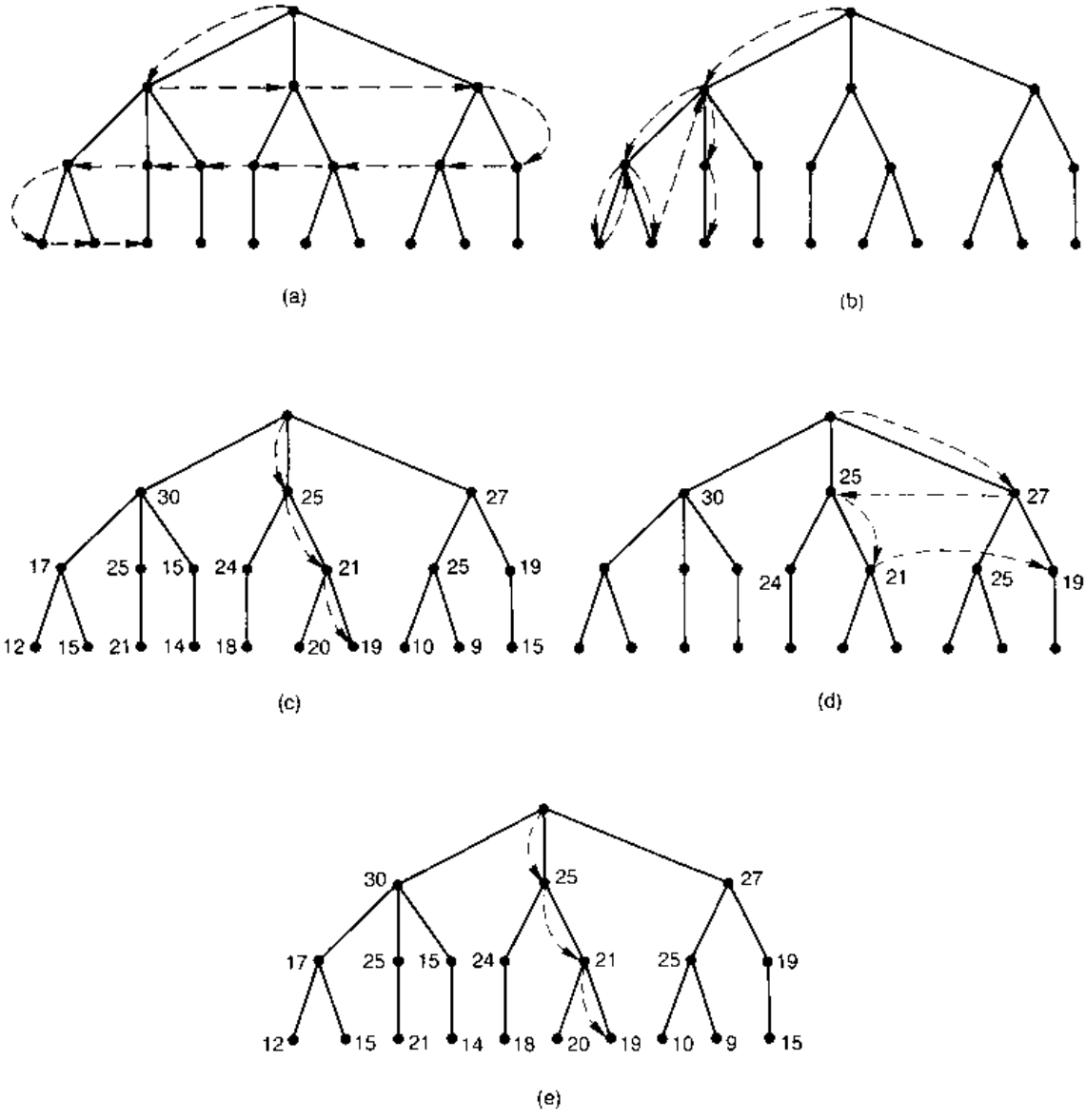


Figure 30.3 *Search through a goal tree: (a) breadth-first search; (b) depth-first search; (c) hill-climbing; (d) beam search; (e) best first search*

30.13.13 A* algorithm

The A* algorithm is a special form of branch-and-bound search which utilizes instead of the path length from the start to the current node the total path length from the start to the goal node. This means that it must possess a heuristic for estimating the distance between the current and the goal node. If this estimate is a lower bound on the actual distance, the solution obtained is optimal. This condition is known as the admissibility of the algorithm.

30.13.14 Games search

Games differ from other problems handled in AI in that there is an active opponent. This has led to the development of specialized forms of search for game playing. The tree through which the search is conducted is known as a game tree. The head of the tree is the start position and the successive layers represent the 'turns' of the two players. Game trees are considered further in Section 30.15.

30.13.15 Move generation and evaluation

A particular form of heuristic search which has been developed for games such as checkers and chess is move generation and position evaluation. Some of the heuristics for these are described in Section 30.15.

30.13.16 Minimax method

The Minimax method utilizes the concepts of move generation and position evaluation and searches for the moves most likely to win the game.

The two players seek to achieve conflicting goals. One player is taken as seeking to maximize the evaluation function and the other as seeking to minimize it. The maximizing player (Max) has to assume that, when it is his turn, the minimizing player (Min) will select that move which minimizes the function.

It is assumed in the Minimax method that it is practical to perform only a limited evaluation of a position; in other words, that it is practical to look only a limited number of moves ahead. The maximum number of levels to which the search can be extended before evaluation takes place is the lookahead depth.

For a start which is Max's move, the even numbered levels contain nodes where the evaluation function is applied to obtain a maximum score and the odd numbered levels nodes where it is applied to obtain a minimum score. A move is evaluated by backing up from the current node to the start, summing the scores at each level. The best move for Max is then that with the maximum backed-up value.

30.13.17 Alpha beta method

Another search method used for game playing is the alpha beta method. It is essentially a form of the Minimax method which prunes those branches of the tree that give a bad result and are therefore irrelevant. The essential principle is that if the opponent has even one good response to a move which would cause it to give a bad result, the move is bad and that branch is pruned.

30.13.18 Control

In general, search needs to be subject to some control strategy. The methods just described in effect constitute particular strategies. However, problems differ, and a strategy suitable for one may not be appropriate for another. The development of search control strategies is an important area of work in AI.

30.13.19 Dependency-directed backtracking

One of the most widely used search methods is depth-first search. This involves backtracking, which unless guided can be an inefficient process. One common method of providing such guidance is dependency-directed backtracking (DDB).

In conventional backtracking, on failing to find a solution the search tracks back to the last node visited at which an alternative path exists. In dependency-directed backtracking, the search returns instead to the node which is implicated in the failure. In this case the backtracking is guided by the data dependencies of the rules involved, which it uses to seek out the node causing the contradiction. This function may be performed by the truth maintenance system.

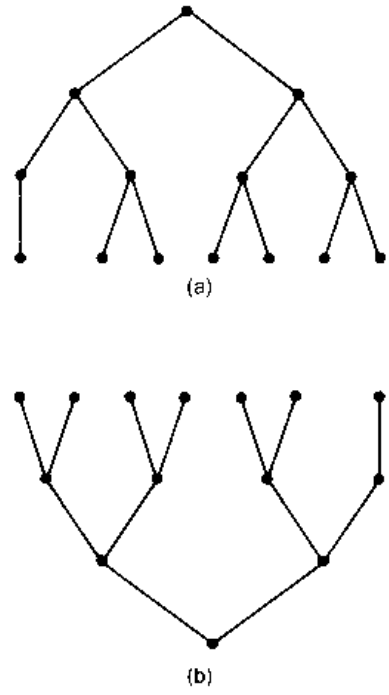


Figure 30.4 *Direction of chaining as a function of the shape of the goal tree: (a) forward chaining; (b) backward chaining. In each diagram the search is from the bottom*

30.13.20 Forward and backward chaining

Search may proceed by forward chaining or by backward chaining. These two modes of search may be explained either in terms of the rules or of the search tree.

In forward chaining the left-hand side of the rule is instantiated first, so that this mode is termed data-driven inference. In backward chaining, by contrast, the right-hand side of the rule is instantiated first, and this mode is termed goal-driven inference. In terms of the search tree, forward chaining involves a search from the bottom to the top of the tree, or from leaf to root, whilst backward chaining involves a search from the top down, or from root to leaf. Thus forward chaining is referred to as data-driven or bottom-up, or as antecedent reasoning, and backward chaining as goal-driven, top down, or as consequent reasoning.

The mode of chaining which is most appropriate depends on the shape of the tree. Figure 30.4 shows two search trees. Forward chaining is best suited to the fan-in case shown in Figure 30.4(a) and backward chaining to the fan-out case shown in Figure 30.4(b).

30.14 Matching and Pattern Recognition

30.14.1 Matching

Another major activity in AI, and one closely related to search, is matching. Some form of matching is involved in virtually all AI work but the nature of the matching

process depends on the particular field of application. Areas of AI in which matching is required include logical reasoning, learning, planning, expert systems, vision and natural language comprehension.

Matching is required for a number of purposes. It may serve to identify and classify objects, retrieve objects from a knowledge base, establish the eligibility of objects for inheritance, select alternatives, control a sequence of operations, and so on.

The overall process of matching may be described as one of representation, transformation and comparison. The object to be matched must first be represented in a form which captures the relevant characteristics. This representation may then need to be transformed to make it conformable for comparison with another object, the referrent. This comparison is based on a matching measure, or metric, which forms the basis of comparison, and a matching criterion, which is used to decide whether a match is established.

There is a variety of representational structures to which matching may be applied. They include: clauses in propositional or predicate logic and logic rules; sets and bags; frames and scripts; and graphs, trees and networks.

There are a number of types of matching metric. There are various distance metrics based on quantitative variables. They may be deterministic or probabilistic. Probability metrics include product moment correlation and measures of clustering. There are also distance metrics based on qualitative variables. These variables may be: binary variables, denoting one of two states; nominal variables, denoting equality or inequality; and ordinal variables, denoting rank order.

There are a number of similarity measures. One type of similarity measure is based on the sets of attributes common to the object and its referrent. Another type which is used for labelled graphs is based on the 'cost' of transforming the graph into its referrent graph. Another metric is the distance which can be defined between the fuzzy sets associated with an object and those associated its referrent. The matching criteria used, and the types of matching obtained, may be exact, partial or fuzzy.

30.14.2 Pattern recognition

Pattern recognition comprehends, but is somewhat broader than, matching. The term is applied particularly to vision. The process of pattern recognition involves feature selection, matching and classification. Pattern recognition is often closely associated with learning by the development of classification rules. Pattern recognition is one of the strengths of neural networks, described in Section 30.21.

30.15 Problem-solving and Games

An important part in the development of AI has been played by problem-solving of various kinds, particularly puzzles and games. An influential early program was General Problem Solver (GPS).

30.15.1 Puzzles

Puzzles frequently quoted in the AI literature include missionaries and cannibals, painted squares, the travelling salesman and the Towers of Hanoi (or Hanoi Towers) problems. The solution of these puzzles is treated essentially as a search. A particular form of search applied to puzzles is means–ends analysis.

In the Towers of Hanoi the goal is to transfer three graded discs from one peg to another, starting from an initial state in which the three discs are on one peg, with the smallest disc on top and the largest at the bottom, and there are two empty pegs. The rules are that a disc can be moved only when there is no disc on top of it and that it may not be placed on a smaller disc at the destination peg. The puzzle is therefore a planning problem in a world akin to the blocks world described below.

30.15.2 Games

Games likewise feature strongly in AI. These are generally two-person, zero-sum games, and include tic-tac-toe (noughts and crosses), checkers (drafts) and chess. These may all be treated as board games and have well-defined rules. Such games are generally represented by a game tree, with the first state at the root of the tree and with the successive move options represented by the successive plies below.

For any but the simplest game, a blind search is impractical for combinatorial reasons and some more sophisticated search method is needed. As already described, characteristic search methods used for game tree searches include the Minimax and alpha beta methods.

Practical problems may be handled by a games approach insofar as they can be treated as games against nature; in particular, against a nature which seeks to defeat the human player by invoking Murphy's law that whatever can go wrong, will go wrong.

30.15.3 Samuel's checkers program

An early and influential games program was the checkers program of Samuel (1959, 1963a,b). This program used Minimax search and heuristic methods for state evaluation and move generation. State evaluation utilized a function with some 16 features such as the number of pieces, piece location and piece advantage. Move generation was guided by tree pruning heuristics. The program also possessed a learning capability, with storage and retrieval of board states which had occurred in previous games.

30.15.4 Chess playing programs

Another game which received attention early in the work on AI and has been influential in its development is chess. Work on computer chess is described in *Computer Chess* (Newborn, 1975). A short account of its historical development is given by Charniak and McDermott (1985).

Early workers in computer chess were C.E. Shannon (1950a,b) and Turing (1953). An early program was written by Bernstein. A major advance occurred in 1967 with the program by Greenblatt. Another influential treatment was that of Newell and Simon (1972).

The general approach to chessplaying is broadly similar to that applied to checkers, as just described. A search is conducted through the game tree using methods such as Minimax and alpha beta, and exploiting heuristics for state evaluation and move generation.

The conduct of a game such as a chess may be regarded as form of planning, albeit under conditions where there is an opponent who seeks to frustrate the plan.

30.15.5 GPS

General Problem Solver (GPS) by Newell and Simon (1963) was another early and influential program. It is described in *GPS: A Case Study in Generality and Problem-Solving* (Ernst and Newell, 1969).

GPS may be regarded as the first AI system to make a clear separation between problem-solving and task knowledge. It was designed to tackle the class of problems which can be formulated in terms of a set of objects, which include states, and of operators which are applied to these objects to transform them into goal objects, or states.

The basic method used in GPS is means–ends analysis. The search is depth-first, with backtracking, and utilizes forward chaining.

In GPS an operator has three features: the preconditions, the transformation function and the differences reduced. The first is a state description which it is a necessary condition that the current state should match for the operator to be applicable. The second is the function which the operator performs. The third links the operator to the differences which it is effective in reducing.

30.15.6 Blocks world

An environment widely studied in AI work is the so-called blocks world. This world consists of a set of blocks on a flat surface. It is a world which is relatively simple and predictable.

Blocks world has been used as an object of study in several areas of AI. It has obvious application to manipulation by robots, but it has also been used in work on computer vision.

30.16 Vision

A quite different area of work is that of vision. This topic is a major one in AI but is not of prime concern here, and will be treated briefly.

Accounts of visual image processing and computer vision are given in *Computer Techniques in Image Processing* (Andrews, 1970), *Computer Vision Systems* (Hanson and Riseman, 1978), *Computer Vision* (Ballard and Brown, 1982), *Vision* (Marr, 1982), *Robot Vision* (Horn, 1986) and by Winston (1984), Patterson (1990) and Tanimoto (1990).

Most applications of visual image processing lie outside the process field, but its use in robotics may have some bearing. There are also applications in accident investigation, as described below.

Visual image processing is generally described as involving an image acquisition stage followed by low level, intermediate and high level processing stages. The image acquisition stage yields a digitization of the image. Low level processing deals with noise reduction, outline and edge definition, thresholding, and texture and colour. Thresholding converts a grey image into one with regions of black and white only. Intermediate level processing handles shape formation and interpretation and involves operations such as connecting, filling in, combining boundaries, determining regions and assigning labels. High level processing deals with semantic analysis and interpretation and involves the identification and characterization of objects and relationships. The various processes utilize a number of specialized techniques such as the determination of the edge distance and surface direction, region growing, shape analysis, and so on. More advanced topics include three-dimensional images and motion. Work on aspects of visual image processing, notably on blocks world problems, has had influence on AI generally.

Image enhancement may sometimes be used in accident investigation. The Piper Alpha Inquiry heard evidence on image enhancement of photographs taken of the west side of the platform in the early stages of the fire, with particular reference to the issues of the nature and source of the fireball and of any damage which may have occurred to the firewall between the modules, though in the event it was not possible in this case to take much from this evidence.

30.17 Natural Language

Another area of work is that of natural language. This too is a major topic in AI, but again one which can be treated briefly here.

Accounts of natural language processing and machine translation are given in *Syntactic Structures* (Chomsky, 1957), *Semantic Information Processing* (Minsky, 1968), *Understanding Natural Language* (Winograd, 1972), *Semantics* (Lyons, 1977), *Syntax* (Culicover, 1982), *Practical Experience of Machine Translation* (Lawson, 1982), *Language as a Cognitive Process* (Winograd,, 1983), *Language Learnability and Language Development* (Pinker, 1984), *Conceptual Structure* (Sowa, 1984), *Natural Language Processing* (Cullingford, 1986), *Understanding Natural Language* (J. Allen, 1987) and by Winston (1984), Charniak and McDermott (1985), Patterson (1990) and Tanimoto (1990).

Natural language processing as such is of little interest here, but work in this area has an important bearing on topics which are relevant such as knowledge and knowledge representation. Work on natural language covers areas such grammars, parsing, syntax, semantics and language generation.

Some kinds of knowledge used in understanding language include: syntax, or the structure of language; semantics, or the meaning of language; pragmatic knowledge, which relates sentences and their meaning to context; and world knowledge, which is required to use a language effectively.

In the areas of semantics, work relevant to the topics discussed earlier includes that on the semantics of quantity, time, space, and knowing and belief.

Transition networks, a technique for parsing sentences, and their development, augmented transition networks (ATNs), are based on directed graphs. ATNs have been used in Stone World, a program which simulates some of the activities of a stonemason, moving objects around an environment.

Some understanding of natural language is likely to be helpful in applying AI techniques in areas such as operating procedures.

30.18 Planning

Another major area of work in AI is that of planning.

Accounts of AI planning include those in *GPS* (Ernst and Newell, 1969), *A Structure for Plans and Behavior* (Sacerdoti, 1975), *Planning and Understanding* (Wilensky, 1983) and *Readings in Planning* (J. Allen, Hendler and Tate, 1990) and by Fikes and Nilsson (1971), Tate (1976, 1977), Sacerdoti (1977, 1985), Waldinger (1977), Stefik (1981), Vere (1983, 1992), Winston (1984, 1992), Chapman (1985), Charniak and McDermott (1985), Currie and Tate (1991) and Lyons and Hendricks (1992).

Planning programs which have been influential in the development of planning in AI are GPS by Ernst and Newell (1969), STRIPS by Fikes and Nilsson (1971) and Fikes, Hart and Nilsson (1972), NOAH by Sacerdoti (1975, 1977), NONLIN by Tate (1977), MOLGEN by Stefik (1981), DEVISER by Vere (1983) and TWEAK by Chapman (1985).

30.18.1 Planning and plans

Requirements for planning are that there be an initial world state, a set of actions which change that state and a set of goals for the final state, and that the environment be sufficiently predictable, though not necessarily completely determined.

The need for planning arises where the situation is novel or critical. Often, however, the situation is familiar. In such cases it may well be sufficient to retrieve from store an existing plan.

It is instructive to compare a plan and a program. A plan is typically executed once, whilst a program may be run many times, albeit with different input data. A plan may have to cope with an environment which is subject to changes, whereas the environment in which a program operates is stable. A plan defers commitment in order to be able respond to the environment.

Planning may be regarded as a special case of reasoning about time, or temporal reasoning. The temporal relationships may be shown in a time map, which is a specialized form of associative network. In one form of time map the nodes represent times, in another they represent situations.

Planning involves decomposing a task into a set of subtasks. These subtasks are then further decomposed until a level is reached at which a subtask decomposes into a set of primitive actions. The task may be represented in the form of a task network, which is a special kind of time map. The structure of the task is in effect a plan for performing it.

Accounts of the overall activity of planning tend to break it down in different ways. One broad type of activity is plan generation. This involves creating a plan to perform a task. The generation of plans is one of the more difficult areas of planning. Plan generation tends currently to be domain-specific, with domain-independent plan generation often a rather distant goal.

It may not always be necessary to generate a fresh plan. In some cases it is sufficient to recognize that the task is, or is sufficiently close to, one for which a plan has already been devised and is already in store.

Another broad area of planning is plan selection and co-ordination decisions, which are rather more amenable to domain-independent treatment. Plan selection involves choosing from candidate plans and plan co-ordination the sequencing of a set of plans. Criteria for making these decision include avoidance of interference between plans and minimization of resources, including time.

Planning, therefore, involves the manipulation of a number of plans. These plans are not necessarily treated as a global plan. The emphasis may be rather on the planner and on the way in which it manipulates these plans during execution. In general, plans may be relatively simple, but the planning algorithms which manipulate them can be rather complex.

Plan execution involves executing the primitive actions of the plan, monitoring for failures and, if necessary, replanning.

30.18.2 Blocks world and mundane planning

Much AI work on planning has centred around the blocks world situation in which a robot performs actions such as stacking or unstacking the blocks. In the simple case, it is assumed that the only changes to the environment are those caused by the robot's action and that these actions are predictable, instantaneous and performed one at a time.

Features of this situation are the relative simplicity of the goals, the world state and the resultant plans. In real-life, or mundane, situations the case is quite different. There are likely to be a number of goals some of which may conflict and there may be a large amount of common sense information which needs to be taken into account.

30.18.3 Goal ordering and meta-goals

Planning is sensitive to the order in which the goals are attempted. An inappropriate ordering can result in extensive backtracking. Methods of goal ordering are therefore needed.

One method is to permute the order of the goals if there is difficulty in obtaining a solution. A more systematic approach is to order the goals in a hierarchy. High level goals have features such as: they are the most difficult to achieve, they determine the structure of the space, and they are not themselves affected by actions.

In many cases, particularly in mundane situations, the problem of the ordering of goals becomes quite severe. There are multiple goals which may interfere or are conflicting so that there is a need to be able to reconcile goals and to abandon goals. This problem has often been tackled by the use of *ad hoc* rules which set meta-goals such as achieving as many goals as possible, maximizing the value of the goals achieved, avoiding impossible goals and economizing resources such as time.

Wilensky (1983) has attempted a more fundamental approach which eschews this *ad hoc* approach and in which planning of meta-goals, or meta-planning, is conducted in exactly the same way as regular planning of goals. This approach is implemented in the program PANDORA.

30.18.4 Protection of goals

Planning requires that certain goals and states be protected from alteration. It is normal that a goal, once achieved, is protected. However, if subsequently a solution cannot be found, it may be necessary to violate

this protection in order to seek a solution by goal permutation or some other method.

Protection is also applied to states. A state is protected during an interval if it is required to be true throughout that interval. An important class of plan failure is that of protection violations.

One strategy for preventing protection violations is to detect them as they occur. Another is to anticipate them. The basic method of dealing with a protection violation is reordering.

30.18.5 Events, actions and macroactions

The interaction of an agent with an environment may be described in terms of the actions of the agent and of the events in the environment.

The general form of a primitive action routine specifies (1) objects (to be used), (2) steps (to be executed), (3) order (of steps) and (4) protection (of goals).

A primitive action is modelled by specifying the action routine and the pre-conditions and post-conditions of the action, or in other words the conditions for it to be taken and its effects.

A set of primitive actions may be grouped together in a structure with associated goal protections to form a macroaction. The plan implemented by a macroaction is thus one created by a human rather than an AI planner. Macroactions are a useful device, but also have drawbacks. In some cases a macroaction may be inflexible or inappropriate.

30.18.6 Operators

Closely related to the above is the concept of an operator. In AI planning an operator acts on a state to effect transition to some other state. An operator is an action with attached lists of pre-conditions and post-conditions. The pre-conditions are the conditions which must be met for the operator to be applied and the post-conditions those which will then pertain. One of the most widely used operators is the STRIPS operator, described below.

30.18.7 The frame problem

In most cases, when an action in a plan is implemented, only a limited proportion of the system states alters, so that the effect is localized. There may, however, be a large number of states that might change. The need to infer that a state will not change across an event is known as the 'frame problem', the term frame here having no connection with frame as a form for knowledge representation.

30.18.8 Planning by search

In AI, planning is effectively a specialized form of search. There are two approaches which may be taken to this search. One is to search through the space of world situations, or possible states of the world. In this type of search the initial state and final states are given by initial and final world models and the operators are the primitive acts.

The alternative, and generally preferred method, is to search the space of plans. In this case operators are applied to reduce the task to subtasks and primitive tasks and to order unordered tasks. The search is conducted to discover a sequence of operations to transform the initial state into the goal state.

30.18.9 Measures of complexity

A measure of complexity in planning may refer either to the planning algorithm or to the planning task. The computational time for the implementation of a planning algorithm may be expressed in terms of a function $O(n)$, where n is the number of items or some other suitable metric of problem size. If in the algorithm $O(n)$ is a polynomial in n, the problem is said to have polynomial time complexity. If, on the other hand, $O(n)$ is such that n appears as an exponent, the problem is said to have exponential time complexity. The increase in computational time with n for exponential time complexity is such that the task of solution is regarded as intractable, whereas with polynomial time complexity the task may be tractable.

The difficulty of a planning task is commonly expressed in terms of NP-completeness. Known algorithms for the solution of NP-complete problems have an exponential time complexity and the task is generally assumed to be intractable. A task which is difficult in this sense is said to be NP-hard.

30.18.10 Means–ends analysis

One of the basic techniques of planning is means–ends analysis. The essential features are an initial state, a goal state, a set of operators with pre-conditions, and a difference function. The latter is a measure of the difference between the goal state and the current state.

Means–end analysis starts with a small number of general steps which are then expanded into more detailed steps. If in the current state an operator cannot be applied because a pre-condition is not satisfied, the algorithm creates a subgoal. It moves to an adjacent state in which the pre-condition is satisfied.

One problem in means–ends analysis is that of real and apparent difference, or distance from the goal. If the difference function is crude and inappropriate, the search can enter a dead end where the apparent distance to the goal is short but the real distance is large. An analogy is reaching a point which is close to the goal as the crow flies but where the path is blocked by an insurmountable cliff face.

30.18.11 GPS

Mention has already been made of the General Problem Solver (GPS) program of Ernst and Newell (1969). The basic method used in GPS is means–ends analysis. GPS works from the current state to the goal in a forward-chaining process. It proceeds by selecting and applying operators to reduce the difference function. If necessary, it resorts to the creation of subgoals. If the search reaches a dead end, it backtracks. Thus GPS in effect uses a depth-first search.

30.18.12 STRIPS

A development from GPS is the planner STRIPS (Standford Research Institute Problem Solver) created by Fikes and Nilsson (1971) and Fikes, Hart and Nilsson (1972). STRIPS has had a major influence on AI planning, being widely used, copied and modified. STRIPS is a linear planner, as described below.

A characteristic feature of STRIPS is the operator used. The STRIPS operator consists of an action with a specified list of pre-conditions and post-conditions. The pre-conditions are the conditions which must be met for

the operator to be applied and the post-conditions those which will then pertain.

Another feature of STRIPS is that it tackles the frame problem by making the default assumption that an action has the effects specified, no less and no more.

30.18.13 Linear and non-linear planning

A distinction is made in planning between linear and non-linear planning. Early planning programs used linear plans. The planner starts at one end, either the initial or the goal state, and moves step by step closer to the other end. The order of the operations performed is completely specified. Non-linear planning, by contrast, utilizes partial plans. A partial plan is a set of steps which is not fully determined. Features of a partial plan which may not be fully specified are the order of the steps or the choice of operator to be used. A single partial plan may comprehend a number of total plans, or completions.

The use of non-linear instead of linear planning is much more efficient, being characterized by polynomial time, as opposed to exponential time, complexity.

30.18.14 NOAH

The first non-linear planner was NOAH by Sacerdoti (1975, 1977).

30.18.15 Planning theorems

A feature of AI planning is the formulation of governing theorems. This aspect is associated particularly with the work of Chapman. This work moves planning away from *ad hoc* approaches and emphasizes the proving of planning theorems, on correctness or attainability.

30.18.16 TWEAK

The planning theorem approach is embodied in the TWEAK program developed by Chapman (1985). This is a non-linear planner which retains the STRIPS-type operator. A plan produced by the program is guaranteed to be correct.

30.18.17 Hierarchical planning

In the foregoing account frequent reference has been made to goals and some to subgoals. It might perhaps be inferred from this that AI planning always involves a hierarchy of goals, but this is not so. Hierarchical planning is only one approach.

In hierarchical planning the higher level goals are expressed in relatively general terms and are then expanded into the more detailed lower level goals. Translation from higher to lower levels goals is a matter of inference. To this extent hierarchical planning may be distinguished from planning proper, which involves the selection and ordering of goals.

30.18.18 Non-subgoaling planning

An alternative to hierarchical planning is to use a single level of goals. Such non-hierarchical planning is sometimes known as non-subgoaling planning. The characteristic non-subgoaling planner proceeds by forward chaining using means–ends analysis and adds actions to the plan in the order in which they will be used. Using this approach it is relatively easy to check that the current plan does not enter into an undesirable state, and hence that the final plan does not do so either.

30.18.19 State graph planning

In state graph planning the problem is represented as a graph of the possible states of the system, the states being represented by the nodes and the actions by the arcs connecting the nodes. State graph planning can provide solutions to a wide range of planning problems, including most operating procedure synthesis problems.

However, it has a number of limitations. Problems of modelling and of undesirable states have to solved by the user in the process of creating the state graph. The state graph can be very large and it may not be easy to modify it. There are issues of the correctness and completeness of the stage graph.

30.18.20 Goals of protection

A planner should ensure that entry is not made into an undesirable state. However, AI planning methods for the avoidance of such states are not well developed. Hence in applying such planning to process problems such as operating procedure synthesis, where it is essential to avoid unsafe states, some adaptation is necessary.

A variety of terms have been used to describe the negative goal of avoiding entry into an undesirable state. They include domain constraints, avoidance goals, preservation goals and goals of prevention. The latter term is the one used here.

30.18.21 Functional operators

As already described, a central concept in planning is that of an operator. Reference has been made particularly to the STRIPS operator, which has been widely used. However, in systems such as process networks the conditions after an event can depend on those which pertain before it. In other words there is a functional dependency between the input and output states. This cannot be handled by a STRIPS-type operator.

This problem has led to the development of the conditional, or functional, operator. This type of operator has a number of sets of pre-conditions and a number of sets of post-conditions. For each set of pre-conditions, there is a corresponding set of post-conditions which apply.

30.18.22 Action synergy

It commonly occurs in planning that a group of actions has an effect which is not exhibited by the individual actions taken in isolation. This is known as action synergy.

A simple example is a pair of valves in a pipe. If the initial state is that both are closed, the action of opening one of them does not have the effect of allowing flow through the pipe. This effect is obtained only by the actions of opening both valves.

There are there thus some goals which can be achieved only by action synergy. Action synergy may also be the cause of an undesirable effect. In some cases it can have the effect of entering an unsafe state.

30.18.23 Subplan merging

Another situation common in planning is the need to merge two subplans. This can often be a non-trivial operation.

A simple example of the need for subplan merging is the problem of taking a tool from a toolbox. The initial states are that the toolbox is shut and that the tool is

inside. The desired end state is that the toolbox is shut and that the tool is outside. The last two states therefore constitute goals for the end state. The plan must ensure that the two subplans for removing the tool and shutting the toolbox are so merged that the tool is removed before the toolbox is shut.

30.18.24 Planner operation

At this point an account is given, following Vere (1992), of the operation of a typical AI planner. The planner operates by keeping a stack of goals and conducting an ordered depth-first search to achieve them.

It proceeds by a process of node expansion, involving backward chaining. Each node represents a subgoal. The planner achieves the subgoal by selecting an action with a post-condition which matches the subgoal. The pre-conditions of that action then become the new subgoals.

It is not always necessary or appropriate to expand a pre-condition. In many cases a pre-condition can be achieved by linking. Linking is used where the pre-condition of a subgoal is already satisfied, in that there already exists elsewhere in the plan above the current subgoal a node with an assertion which achieves that pre-condition. In some instances there may be several linkings which satisfy a pre-condition. Associated with this are syntactic conventions in action descriptors which inhibit backward chaining of a pre-condition and thus reduce the extent of backtracking.

Where node expansion throws up more than one candidate action, in other words where an OR branch occurs, it is necessary to select one of them. Rules are therefore required for action selection. These rules may be domain-independent or domain-specific. Some criteria for domain-independent selection are to choose an action on the basis of: the number of non-linkable pre-conditions; the number of additional, or bonus, goals which it achieves; and the resources which it consumes.

Conflict can arise where there are two unordered nodes with contradictory assertions. Resolution of the conflict needs to be made immediately. It is effected by placing the two nodes in order and maintaining the protection of the upper node.

Node expansion, linking and conflict resolution by ordering are the three fundamental operations of this type of planner. Vere gives an example of a blocks world plan utilizing only these three operations. If neither node expansion nor linking is possible, the subgoal cannot be achieved and it then becomes necessary to backtrack.

30.18.25 NONLIN

The program NONLIN by Tate (1976) is a hierarchical planner which operates broadly on the above lines and has been applied to turbine overhaul and naval missions.

30.18.26 Execution monitoring

A plan may fail in execution due to a number of causes. One such cause is simply random events. Hence execution monitoring is an essential part of planning. Planning of a task and its execution need to be interleaved. There is no point in formulating a comprehensive plan if it is likely to be negated by events occurring at an early stage. On the other hand, some degree of forward planning is desirable. One issue in planning is how far ahead to plan.

There is no agreed approach to execution monitoring, but it is possible to identify certain issues. At any given time the planner has an expectation that a number of states are true. It may conduct tests to verify them. In this case it requires criteria for selecting the tests.

A related problem is the explanation of unexpected results. These may arise for a number of reasons such as a defective model of the world situation or a random event.

30.18.27 Reactive planning

The conventional approach to planning is the creation of a plan which in the absence of changes in the environment will achieve the goals but which has some capability to respond to such changes and to replan. There exists, however, a quite different approach, which is to achieve goals by a process of responding to the environment. This is reactive planning, which is described by Lyons and Hendricks (1992).

Conventional planning has typically been applied to situations of the blocks world type. Other worlds exist, however, and need to be dealt with. One envisioned by Schoppers (1987) is 'baby world', in which the environment is disturbed by activities characteristic of babies, such as throwing bricks around, and so on. It is with this type of world that reactive planning is concerned.

Like conventional planning, reactive planning seeks to achieve goals, but when a change in the environment occurs, it reacts not by making a modest change to the original plan, or replanning, so much as by creating a new plan.

Thus the techniques used in reactive planning are based on some form of reaction between the agent and the environment. For example, Brooks (1986, 1989) has used a hierarchy of routines which react with the environment to achieve goals, the hierarchy being termed the 'subsumption architecture' and the routines the 'behaviours'.

Another aspect of reactive planning is the work of Nilsson (1988), who has addressed the problem that in conventional planning the higher levels surrender control and have to suspend action until they receive it back, so that the situation is liable to occur that the lower levels of control continue with activities which have been rendered inappropriate by a change in the environment.

Reactive planning is a relatively new but now influential approach.

30.18.28 Temporal planning

Planning necessarily deals with the ordering of subtasks, but it does not necessarily deal with time constraints. Temporal planning addresses problems where such time constraints exist.

These time constraints have been handled in work by Vere (1983), in which each action is assigned a start time and a duration. Temporal relationships are defined using words such as before, equal, meets (adjoins), overlaps, during, etc. He has implemented this method in the program DEVISER.

30.18.29 Domain dependency

Initial work on planning utilized domain-independent approaches. Later work has moved to domain-dependent methods. This change of approach was prompted by experience. In addition, however, it has been shown by

Chapman (1985) that there are theoretical reasons for thinking that it is not practical to build a domain-independent planner which is able to tackle real-life problems and is also provably correct.

30.18.30 Decision theory

One method of analysing a plan is the use of decision theory. Since AI work on planning has largely been concerned with synthesis and since decision theory is a tool for analysis, the extent of application of decision theory in planning has been limited. Human planners are well able to create plans in mundane situations. Decision theory was developed to assist in the analysis of plans for the more complex cases.

More extensive application of decision theory for the analysis of plans synthesized by AI planning methods is likely to highlight the problem of obtaining estimates for the values of probability and utility used in the theory.

30.19 Learning

From the earliest day of AI, the creation of a machine which can learn has been one of the principal goals. Accounts of learning in AI are given in *Learning Machines* (Nilsson, 1965), *Machine Learning* (Michalski, Carbonell and Mitchell, 1983–) and by Lenat (1982, 1983) and Simon (1983).

Two principal categories of task in machine learning are (1) classification and (2) problem-solving.

The representation of the objects which the machine experiences may take various forms. Objects may be described in various ways, including in terms of binary features, multi-valued attributes, classes or structural relationships.

Learning may be classified in a number of ways. The learning modes considered here may be described as (1) learning by instruction, (2) learning by classification, (3) learning by exploration and conceptualization, (4) learning by experience and analogy, (5) learning from failure, and (6) learning by problem-solving.

In addition to these learning modes, there are also particular devices that have a learning capability. Two which figure prominently in AI are (1) neural networks and (2) genetic algorithms.

Of particular importance in learning is the use of inference by induction and this is discussed in Section 30.20.

In the following an account is given of the learning modes and learning devices just described. It needs to be said, however, that for some of the learning modes the work described constitutes only a very partial exploration of the mode both in breadth and depth.

30.19.1 Supervised and unsupervised learning

Most work on classification tasks involves supervised learning. Typically the program is given a learning set in which both the class and attributes of each object are specified and it is then required to create a discrimination hierarchy.

There is some work, however, on learning in unsupervised classification tasks where the program has to perform the assignment to classes itself.

In problem-solving unsupervised learning is the norm, but some work has been done on supervised learning in which an expert prompts the program at crucial junctures.

30.19.2 Learning from data and stored knowledge

Another distinction is between learning from data and from stored knowledge. It is often assumed that learning requires new data about the interaction of the agent and its environment. In fact, there is generally much to be learned from knowledge already in store which can be retrieved and processed in various ways so as to learn new concepts, rules and so on. In particular, learning may take place in the course of problem-solving.

30.19.3 Learning by instruction

One method by which a program may learn is to receive instruction from a tutor. Such learning by instruction may proceed in various ways.

One type of instruction which the tutor may give is modifications or additions to rules such as those in the knowledge base of an expert system. The tutor may provide additional rules, perhaps rules-of-thumb. Or he may monitor the responses of the system, detect deficiencies in these responses, examine the explanations given for them, and identify and modify the rules causing these defective responses.

Instruction of an expert system on these lines is performed by the expert system TEIRESIUS of R. Davis (1980), created as an intelligent editor for MYCIN. An account of its operation is given by Charniak and McDermott (1985).

There is an element of instruction in some of the other methods of learning also, insofar as the learning set or environment presented to the program has been chosen by the tutor. This choice is often of considerable importance.

30.19.4 Learning by classification

Learning by classification involves inductive reasoning in which generalizations are made from a learning set of specific objects, each of which is labelled with attributes and assigned to a class. This form of learning is considered in more detail in Section 30.20.

30.19.5 Learning by exploration

Learning by exploration is essentially concerned with concepts. The program is given a learning set in which the objects are unclassified and required to develop concepts. One area of work here is conceptual clustering in which the program determines how to cluster and to describe objects. It typically involves the creation of a hierarchy of concepts.

Two programs which perform learning by exploration are AM and EURISKO, both by Lenat (Lenat, 1982, 1983; Lenat and Brown, 1984). Their operation is described by Charniak and McDermott (1985). Exploration differs from search in that the purpose is to develop and enhance concepts rather than to achieve goals. Essentially such exploration involves activities such as determining similarities and differences between objects and classifying them into sets, frames and hierarchies.

30.19.6 Learning by experience

Learning by experience may take various forms, but the aspect which is considered here is essentially learning by analogy. This type of learning is also known as case-based

learning. In such learning, numbers of specific cases are stored in memory. An issue is the extent to abstraction of the salient features is performed at the time of storage or is deferred until the case is to be used. Clearly this affects the storage of cases in, and retrieval from, the memory.

A program which learns by experience is MACBETH by Winston (1980, 1982). An account is given by that author (Winston, 1984). This program deals with the process of learning from situations by analogy with other situations and the discovery of general rules. A situation, or precedent, is presented in the form of a natural language description. This description is transformed using techniques of natural language understanding. This transformation facilitates the creation of a cause structure for the precedent. The precedent has constraints which are to be matched before the precedent can be applied. The precedent is then applied by analogy to other situations where such a match exists and rules are derived. Such reasoning by analogy is liable to deduce rules which are too sweeping, and 'censors' are used to modify the rules by introducing additional conditions.

30.19.7 Learning from failure

A particular form of learning by experience is learning by failure. A type of failure which features strongly in AI is the failure of a plan.

A program which learns by the failure of plans is HACKER by Sussman and Stallman (1975), another influential system. An account is given by Charniak and McDermott (1985). The program has been used in the blocks world environment. It contains a simulated effector system which reports the reason for failure of a particular step in a plan. The program revises the plan on the basis of the report.

The program also has a collection of 'critics' which have the function of criticizing plans. These critics too have an ability to learn, which they do by analysing the experience of failures.

30.19.8 Learning by problem-solving

As stated earlier, learning does not necessarily have to be based on new data; it is also possible to learn by processing stored data. This type of learning is sometimes called analytical learning, as opposed to inductive learning from data.

Accounts of such analytical learning tend to deal particularly with learning by problem-solving. One problem-solving tool which may be learned is a set of rules. The task of problem-solving is performed. Learning from this solution proceeds by identifying the features of the problem and the problem–solution pairs which were used. From this explanation, general rules are derived. This form of analytical learning is also called explanation-based learning.

Besides rules, other features of problem-solving which may be learned include macro-operators and heuristics.

30.19.9 Neural networks

Turning to devices with learning capability, one of the principal developments is neural networks. A neural network is a network of 'neurons' which in a simplified way models the operation of the human brain. It learns from a learning set of input–output patterns. It is in effect a device for learning by experience. A fuller account of neural networks is given in Section 30.21.

30.19.10 Genetic algorithms

Another device described in biological terms is the genetic algorithm, so called from a loose analogy with genetic change in a population. A genetic algorithm utilizes a set of patterns the weighting of which is changed as learning proceeds. In effect the patterns compete and only the fit survive. Genetic algorithms are used both for classification and for problem-solving.

The genetic algorithm method may be applied to the development of rules in a rule-based production system. The weighting of the rules is adjusted to reflect their contribution to desirable behaviour.

In some applications use is made of operators which propose new rules and the exploration conducted is primarily on the effect of different combinations of rule rather than of weightings of individual rules.

30.20 Inductive Learning

A large proportion of learning in AI proceeds by inference through induction. One of the principal uses of induction is the classification of objects, events and situations, but applications of inductive reasoning are much wider than this and extend to concepts, rules and so on. An account of induction in AI is given by Patterson (1990).

The concept underlying inductive learning is the basic logic of inductive inference:

$$\begin{array}{ll} \text{Assertions} & P(a_1) \rightarrow Q(b_1) \\ & P(a_k) \rightarrow Q(b_k) \\ \hline \text{Conclusion} & \forall xy\ P(x) \rightarrow Q(y) \end{array}$$

Induction may be regarded as a process of class formation. The task is to partition the universe U of objects into classes. The minimum partition is into a single class C and the rest U-C. To this end use if made of concepts, a concept being a description or rule which subdivides a set. The target concept is the concept which classifies all the objects in the universe. The positive instances are those objects which fit the target concept and the negative instances are those which do not. A consistent classification rule is one which is true for all positive instances and false for all negative instances.

30.20.1 Generalization and specialization

There are a number of recognized techniques of induction involving generalization and its converse, specialization. The basic process in induction is generalization. However, generalization may become too sweeping, so that the class created includes negative as well as positive instances. Such overgeneralization may be corrected by specialization.

Methods of generalization are exemplified by the techniques of changing constants to variables, dropping conditions and closing an interval. Replacement of constants by variables simply means that, given that a relation holds in a number of instances, it is inferred that it is generally true. Dropping a condition involves removing a condition in a description and thus widening

the class. In closing an interval it is inferred that what is true of objects at the two bounds of the interval is true of objects in between.

30.20.2 Inductive bias

Generalization may be treated as a search problem. As such, it involves the familiar need to attend to the efficiency of the search. The term bias is applied in this context to those factors, other than those of the learning set, which influence the selection of hypotheses. One type of bias involves restricting the hypothesis space to be searched. Another involves ranking the hypotheses.

30.20.3 Classification

A principal application of inductive learning is classification, in which the program is presented with a learning set of objects each of which is assigned to a class and described by a number of attributes. The task is then to induce a discrimination hierarchy, or a set of rules, for the assignment of the objects to the classes.

In the more straightforward cases the learning set is consistent in that it does not contain counter-examples. More advanced work addresses the problem of such noisy learning sets.

In using a classification algorithm, the selection of the learning set requires some care to ensure that the set provides comprehensive coverage of the domain of interest and, where necessary, to exclude counter-examples.

30.20.4 ID3

One of the principal classification methods is the ID3 algorithm of Quinlan (1983a,b). ID3 is based on an information theory approach.

If in a sample of n objects there is a proportion p which belong to class C and hence a proportion $(1-p)$ which do not, a quantity H_c may be defined as

$$H_c = -p \log_2 p - (1-p) \log_2 (1-p) \qquad [30.20.1a]$$

$$= -\Sigma p_i \log_2 p_i \qquad [30.20.1b]$$

H_c may be regarded as the expected information content of a message from a discrimination, or decision, tree for a set C of objects.

The attribute on which to branch first is selected on the criterion that the information gain is to be maximized. The information gain G_j for attribute j is

$$G_j = H_c - H_j \qquad [30.20.2]$$

with

$$H_j = \Sigma p_i H_{jk} \qquad [30.20.3]$$

$$H_{jk} = -p_{jk} \log_2 p_{jk} - (1-p_{jk}) \log_2 (1-p_{jk}) \qquad [30.20.4]$$

where H_j is the information content at the node for attribute j, H_{jk} is the information content associated with the individual branches at the node, and p_{jk} is the proportion of objects having attribute j in branch k at the node.

The algorithm is illustrated by Quinlan using the following single-class classification problem. Objects either belong to the class or they do not and are then denoted by + or −, respectively. There are three attributes: height, hair and eyes. The learning set of objects is:

short, blond, blue: +	short, dark, blue: −	tall, dark, brown: −
tall, blond, brown: −	tall, dark, blue: −	short, blond, brown: −
tall, red, blue: +	tall, blond, blue: +	

There are therefore three branch points in the decision tree.

Then, since there are three objects out of eight which are in class C, and five which are not, Equation 30.20.1 gives

$$H_c = -3/8 \log_2(3/8) - 5/8 \log_2(5/8) = 0.954 \text{ bits}$$

Taking the first attribute, height, the information still needed for a rule for the 'tall' branch is, from Equation 30.20.4,

$$H_{j1} = -2/5 \log_2(2/5) - 3/5 \log_2(3/5) = 0.971 \text{ bits}$$

and that needed for the 'short' branch is

$$H_{j2} = -1/3 \log_2(1/3) - 2/3 \log_2(2/3) = 0.918 \text{ bits}$$

and hence from Equation 30.20.3 the expected information content is

$$H_j = 5/8 \times 0.971 + 3/8 \times 0.918 = 0.951 \text{ bits}$$

Then from Equation 30.20.2 the information gain is

$$G_j = 0.954 - 0.951 = 0.003$$

This value is negligible. Computing the information gains for the second attribute, hair, and the third attribute, eyes, in the same way yields information gains of 0.454 and 0.347, respectively. Thus the second attribute, hair, is selected for the first branch. Then the first branch of the decision tree is:

Node	*Link*
hair:	red: tall, red, blue: +
	dark: short, dark, blue: − tall, dark, blue: − tall, dark, brown: −
	blond: short, blond, blue: + tall, blond, brown: − tall, blond, blue: + short, blond, brown: −

Proceeding in a similar manner, the third attribute, eyes, is selected for the second branch. This then gives:

Node	*Link*	*Node*	*Link*
hair:	red: tall, red, blue: +		
	dark: short, dark, blue: – tall, dark, blue: – tall, dark, brown: –		
	blond:	eyes:	blue: short, blond, blue: + tall, blond, blue: + brown: tall, blond, brown: – short, blond, brown: –

A further, more complex example is given by Patterson (1990).

Further work on this algorithm has addressed aspects such as handling the noise in the data, the detection of thresholds for numeric attributes and up-dating of the tree with new data.

In one application to the classification of diseases, the algorithm outperformed an expert system constructed by conventional methods over a period of years (Quinlan *et al.*, 1986).

The classification tool EXTRAN is an implementation of ID3.

30.20.5 INDUCE

Another program for inductive learning is INDUCE developed by Michalski and co-workers (Larson and Michalski, 1977; Dietterich and Michalski, 1981). This program discovers class patterns and formulates generalized descriptions of these patterns. A characteristic feature is its utilization for its descriptive language of an extension of first-order predicate logic.

30.21 Neural Networks

A quite different kind of learning device is exemplified by neural networks. These utilize a form of learning which in certain respects mimics that of the human brain. Neural networks are described in *Neural Computing* (Beale and Jackson, 1990) and *Neural Networks in Artificial Intelligence* (Zeidenberg, 1990) and by Patterson (1990) and Tanimoto (1990).

Work on neural networks was originally inspired by research on modelling of the human brain. Another input comes from studies of associationist psychology, particularly behaviourism. A neural network is a large network of nodes connected by links. These nodes are information processing elements based on a simple model of the neuron in the human brain. A node sums the stimuli entering it through the links and has a threshold above which it will execute, or fire, and pass a stimulus to the connected nodes. A link has a weighting which is applied to the stimulus passing along it. The link weights enhance or inhibit the stimuli. The knowledge held in the network is distributed throughout it in the form of features such as these thresholds and weights. The network has an input layer of nodes, an output layer and a number of intermediate layers in between.

Learning in, or 'programming' of, a neural network proceeds broadly as follows. The network is set to its initial condition, typically with thresholds and weights set at random. It is presented with a learning set of pairs of inputs and outputs which it is then taken through. For each input the output is observed and adjustments are made to the thresholds and weights according to some strategy. The process is repeated until the learning set is exhausted.

A common strategy for adjusting the adjustable features during learning is error back-propagation. In this method, the error between the desired and actual outputs is used to adjust first the hidden layer next to the output. This error in then propagated back, ultimately to the input layer. The features most commonly adjusted are the thresholds and weights, but other strategies may be used which involve adjustments to the network topology or even to the learning strategy.

A neural network is a form of statistical associative model. The statistic inference which it utilizes is better able to handle randomness and exceptions than is rule-based inference. Rule-based systems can handle exceptions, but generally at the price of much increased complexity.

Neural networks have been used for knowledge representation, production systems and expert systems, pattern recognition, visual image processing, speech recognition and natural language understanding.

Production systems and expert systems created using the neural network technique are known as connectionist systems. One application, by Touretszky and Hinton (1985), simulates the firing of rules and thus the operation of a production system. Another application is the creation of expert systems, as in the work of Gallant (1988) and Saito and Nakano (1988).

Gallant has described a neural network expert system for the diagnosis and treatment of the medical condition of acute sarcophagal disease. The system handles two forms of disease, six symptoms and three treatments. It is able to make deductions from an incomplete set of data on the symptoms and to give an explanation of the route by which it arrived at its conclusions.

30.22 Graphs, Trees and Networks

AI makes use of a large number of graphs, trees and networks, some of which are now briefly described. Some of these graphical forms constitute forms of knowledge representation, whilst others relate to the reasoning process. The graphical forms can be represented by suitable program structures in the programming languages used. Some graphs, trees and networks used in AI are listed in Table 30.3 and some are shown in Figures 30.2 and 30.5.

Taxonomic hierarchies for classification of entities go by various names. One form of particular importance is the ISA hierarchy, which has been described in Section 30.12 and which is shown in Figure 30.2(b). Another form is the object oriented system (OOS) hierarchy.

An inheritance hierarchy is a particular type of taxonomic hierarchy, which in addition to showing the classification shows also inheritance of attributes.

A discrimination net represents the process of discrimination between entities and attributes in order to identify an object. An object identification net is similar.

Table 30.3 *Some graphs, trees and networks used in artificial intelligence*

Type	*Application*	*Nodes*[a]	*Reference*[b]
Taxonomic hierarchies	Classification	Entities	
All things hierarchy		Entities	Winston, p. 322
ISA hierarchy		Entities	C&M, p. 26
OOS hierarchy	Classification	OOS entities	Patterson, p. 155
Inheritance hierarchy	Inheritance	Entities	C&M, p. 406
Discrimination net,	Identification	Entities; entities,	C&M, p. 154
object identification net		attributes; entities	Patterson, p. 317
Parse tree	Grammar	Syntactic categories	Frost, p. 531
Syntax tree	Grammar	Syntactic categories	Frost, p. 527
Transition network	Grammar	Syntactic categories	C&M, p. 202
Augmented transition network	Grammar	Syntactic categories	
Associative network	Relationships	Entities, attributes	Patterson, p. 129
Semantic net	Relationships	Nouns, verbs, adjectives	Frost, p. 457
Semantic tree	Logical reasoning	Logical expression; truth values	Tanimoto, p. 234
Bayesian network	Bayesian inference	Evidence; inferences; conclusions	C&M, p. 478
Truth maintenance network,	Truth maintenance	Premises, assumptions,	Patterson, p. 85
belief network	systems	facts; beliefs	Winston, p. 244
Constraint propagation network	Constraint propagation	Facts; beliefs	Winston, p. 243
Goal tree	Planning	Goals; subgoals; primitive actions	C&M, p. 277
AND/OR tree	Planning	Goals; subgoals; primitive actions	Winston, p. 39
Search tree	Search	Start; intermediate nodes; end	C&M, p. 265
Games tree	Games	Start; positions; end	C&M, p. 281
Time map	Action sequences	Actions	C&M, p. 432
Task network	Planning	Task; subtasks; primitive actions	C&M, p. 492
Frame network	Frames	Frames	Patterson, p. 138
Decision tree[c]	Decisions	Utility values	C&M, p. 521
Neural network	Neural networks	Model neurons	Patterson, p. 344

[a] Where there is a single entry, all nodes are of this type; where there are two entries (separated by a semi-colon), the first refers to the top node and the second to the intermediate and bottom nodes; and where there are three entries the first refers to the top node, the second to the intermediate nodes and the third to the bottom nodes.
[b] References are to: Charniak and McDermott (1985) (C&M); Frost (1986); Patterson (1990); Tanimoto (1990); and Winston (1984).
[c] The term decision tree is commonly used in AI for a tree which represents decision-making in terms of decision theory, and this is the meaning here.

Also the term 'decision tree' is sometimes applied to this type of diagram.

Diagrams used in the syntactical analysis of natural language include parse trees, syntax trees, transition networks and augmented transition networks (ATNs). A semantic net is used to represent the meaning of sentences.

The associative network is a widely used tool for representing relationships of various kinds, as shown in Figure 30.2(a).

A semantic tree shows the development of a logical expression in terms of its truth values. A Bayesian network gives the structure of the relationships between evidence, inferences and conclusions in Bayesian inference.

A truth maintenance system (TMS), or belief network, shows the structure of the TMS in terms of the current beliefs and the premises, assumptions and facts which support them. A constraint propagation network is somewhat similar.

A goal tree shows the expansion of a goal into its subgoals and ultimately to the primitive actions which are necessary to achieve it. Where AND/OR logic is involved, the diagram may also be referred to as an AND/OR tree. A goal tree is shown in Figure 30.5(a).

A game tree shows the development of a game from the start position, through the moves to the end position. A game tree is shown in Figure 30.5(b).

A search tree shows the process of search from the start through the nodes to a solution, if one is found. Search trees are considered in Section 30.13.

A time map shows a series of actions in time, as shown in Figure 30.5(c).

A task network shows the expansion of a task into its subtasks and ultimately to the primitive actions which

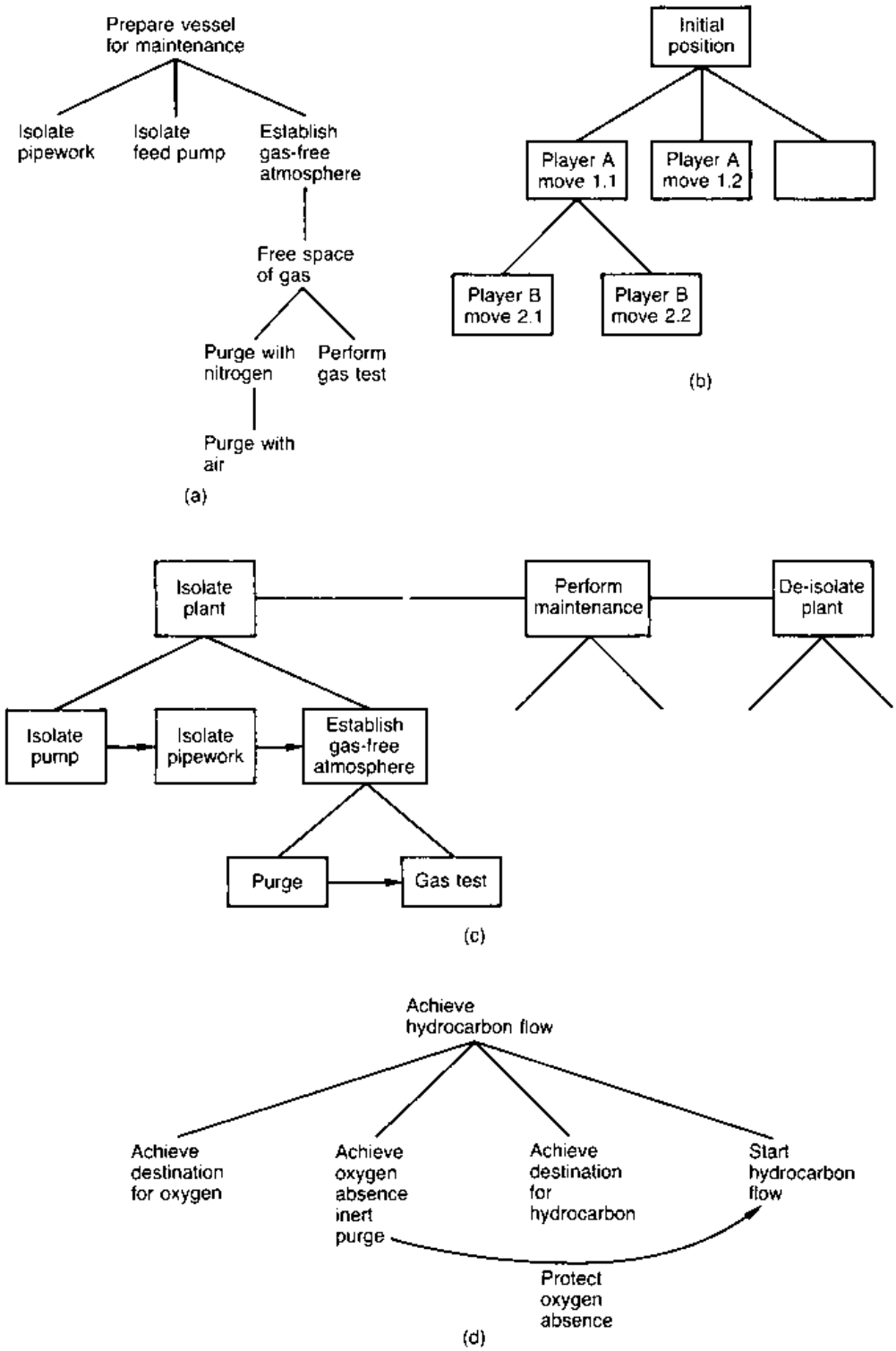


Figure 30.5 *Some graphs, trees and networks used in artificial intelligence: (a) goal tree; (b) game tree; (c) time map; (d) task network. See Figure 30.2 for associative network and ISA forms*

are necessary to perform it. A task network is illustrated in Figure 30.5(d).

A frame tree shows a hierarchy of frames.

The term 'decision tree' is used to describe more than one type of diagram. In terms of decision theory it shows the structure of a decision in relation to the utility values. In other cases the term is applied to discrimination trees. Another, and common, form of decision tree is that used in human decision-making, as described in Chapter 14.

30.23 Directed Graphs

A graphical representation of some importance in engineering is the directed graph, or digraph. Digraphs have been widely used in process modelling. Accounts of directed graphs are given in *Graph Theory in Modern Engineering* (Henley and Williams, 1973), *Structural Models: An Introduction to the Theory of Directed Graphs* (Harary, Norman and Cartwright, 1975) and *Graph Theory* (Gould, 1988).

Directed graphs are also known as directed linear graphs, directed networks or signal flow graphs. A digraph consists of a set of vertices, or nodes, joined by branches, which are also termed links, arcs or edges.

A digraph is said to be connected if it has no pair of vertices which are not connected by branches. It is strongly connected, or strong, if for each vertex there exists a directed path from that vertex to another vertex. Otherwise it is said to be weakly connected, or weak.

A path is a set of at least two connected branches. A closed path is called a cycle, or loop. A digraph which contains no cycles, or loops, is referred to as an acyclic graph. A tree is an acyclic graph.

30.23.1 Flow graph algebra

Three principal rules of flow graph algebra are (1) the addition rule, (2) the transmission rule, and (3) the product rule.

The addition rule states that the value of a variable represented by a vertex is the sum of all the transmittances entering the vertex. The transmission rule states that the value of a variable represented by a vertex is transmitted on every branch leaving the vertex. The product rule states that if a series connected graph has n vertices the $n-1$ branches can be replaced by a single branch whose transmittance function equals the product of the original branches.

The transmittance function, or operator modifying the value leaving one vertex and entering another, is generally a gain constant. Where differential equations are handled, however, it may also be an integration. For an independent variable such as time t this integration may be expressed as $\int dt$, or in the Laplace domain as $1/s$.

A signal flow graph (SFG) is used to represent a set of simultaneous linear algebraic equations or linear differential equations. A typical signal flow graph is shown in Figure 30.6.

These equations may also be cast in matrix form and manipulated in the usual way. Thus SFG theory is a way of modelling system which is not only convenient but has a sound theoretical basis.

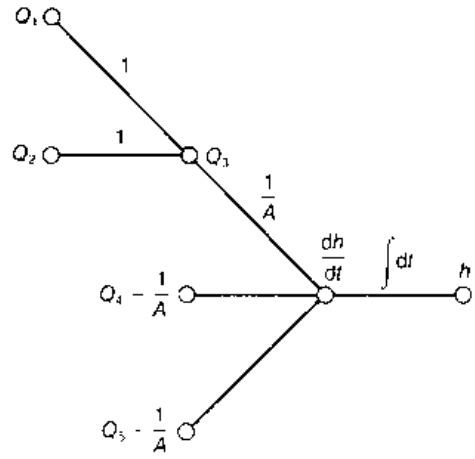


Figure 30.6 *A signal flow graph. Graph for* $Q_3 = Q_1 + Q_2; dh/dt = (1/A)(Q_3 - Q_4 - Q_5); h = \int (dh/dt)dt$

30.23.2 Flow graph reduction

There are a number of techniques for the reduction of SFGs. In addition to the product rule already mentioned, they include elimination of 'self-loops', various elementary transformations and Mason's rule. An account of these techniques is given by Henley and Williams (1973).

30.23.3 Digraphs in process modelling

Extensive use has been made of digraphs in the modelling of process plants, particularly in the modelling of fault propagation. In such work the nodes represent process variables such as flow, pressure, and temperature, and the edges represent the effects of one variable on the other.

In qualitative modelling using digraphs a convention commonly employed is to use a transmittance function of $+1$, 0 and -1 for a positive influence, zero influence and a negative influence, respectively. Some workers also use $+10$ and -10 to denote, respectively, strong positive and negative influences. Another convention often utilized in such work is to denote an AND gate by ⊲.

Generally, it is only certain variables which are of interest. In such cases use may be made of the techniques for the reduction of graphs mentioned earlier.

The use of digraphs in process modelling is discussed further in Section 30.36.

30.24 Expert Systems

One of the AI tools which has been most widely taken up with a view to industrial application is expert systems.

Accounts of expert systems are given in *Building Expert Systems* (Hayes-Roth, Waterman and Lenat, 1983), *Build Your Own Expert System* (Naylor, 1983), *Expert Systems* (Alty and Coombs, 1984), *Expert Systems* (Forsyth, 1984b), *Expert Systems* (Harmon and King, 1985), Expert Systems (Sell, 1985), *Competent Expert Systems* (Keravnou and Johnson, 1986), *Expert Systems: Strategic Implications and Applications,* (Beerel, 1987), *Programmer's Reference Guide to Expert Systems* (Hu, 1987), *Knowledge Acquisition for Expert Systems* (Kidd,

1987), *Building Expert Systems: A Tutorial* (J. Martin and Oxman, 1988), *Artificial Intelligence and Expert Systems* (Savory, 1988), *Expert Knowledge and Explanation: The Knowledge-Language Interface* (Ellis, 1989), and *Expert Systems and Artificial Intelligence: An Information Manager's Guide* (Ford, 1991) and by Winston (1984), Charniak and McDermott (1985), Frost (1986), Patterson (1990) and Tanimoto (1990).

The vast majority of expert systems are rule-based production systems, though other methods can be used such as neural networks.

The description of actual expert systems is deferred to Section 30.25, but occasional reference is made in this section to certain major systems, notably MYCIN.

30.24.1 Project management and organization

The strategic aspects of expert systems are considered in *Expert Systems: Strategic Implications and Applications* (Beerel, 1987).

The management and organization of an expert system project depend very much on the nature and scale of the project. Most industrial applications are relatively modest. For a more substantial project, however, the management and organization may well determine the success.

The selection of an appropriate application is crucial. Some characteristics bearing on suitability are discussed in the next section. There are two essential conditions for undertaking the development of an expert system: that it be feasible and that, once created, it will be used.

The first condition requires that there be available at least one domain expert who can provide the necessary expertize. A decision has to be made whether sole reliance is to be placed on this expert or whether other experts are to be brought in. The function of the experts is not only to furnish expertise, but also to evaluate the system produced.

The second condition, that at the end of the day the system actually be used, implies the involvement of the potential users right from the start. One view is that it is a user who should be responsible for the project. Whether or not this is adopted, the principle of user involvement is not in doubt.

Knowledge acquisition in a project of any size is the responsibility of a knowledge engineer. The knowledge engineer is not a domain expert, but should be skilled both in knowledge acquisition and knowledge representation and in the building of expert systems.

The basic team for the creation of an expert system is thus the project manager, the expert, the knowledge engineer and the user.

30.24.2 Selection of applications

Experience with expert systems indicates that there are some types of problem for which an expert system is suitable and others for which it is not. For the latter, this does not necessarily mean that there is no suitable AI tool, only that an expert system is not that tool.

The most basic requirement is that there be an established domain expertise and an expert from whom the domain knowledge can be elicited.

Another equally basic requirement is that there should be a need for the system so that adequate resources can be made available for its development and so that once it has been developed it is used and maintained.

A distinction is sometimes made between common sense and mundane knowledge, to the effect that common sense involves various forms of reasoning and mundane knowledge various kinds of knowledge about the world. Common sense and mundane knowledge are strong points for humans but weak features of machine intelligence.

The characteristics of a problem which favour an expert system application are: that there is a defined domain of expertise; that the task to be performed is well focused and of moderate complexity; and that the knowledge can be represented in standard forms, particularly by facts and rules.

The task should be one performed by an expert and be of a level of complexity that it is neither trivial nor so involved that creation of an expert system becomes impractical. The time taken to perform such a task is typically between a few minutes and a few days.

In a given organization, the question of the selection of the first application of an expert system is of some importance. As with any other innovation, a bad first experience is likely to set the technology back for some years.

30.24.3 System development

The development of an expert system proceeds through the following typical stages: (1) system concept, (2) feasibility study, (3) outline specification, (4) preliminary knowledge acquisition, (5) knowledge representation, (6) tool selection, (7) prototype development, (8) main knowledge acquisition, (9) revised specification, (10) system development, (11) testing and evaluation and (12) handover. The process is an iterative one, with looping back between some of these stages.

Prototyping covers the creation of the prototype, the writing of the documentation, the induction of the user, and use and evaluation by the user.

The point has already been made that the user should be involved from the start. This involvement should cover not only the specification and evaluation of the final system, but also evaluation at intermediate stages.

An account of the development of a large expert system is given by J. Martin and Oxman (1988).

30.24.4 System architecture and facilities

A minimal architecture for an expert system is a knowledge base, an inference engine and a user interface.

The knowledge base contains the set of facts and rules which constitutes the expertise. A distinction is sometimes made between a database of facts and a knowledge base containing rules. The knowledge base itself is frequently spoken of in terms of a set of knowledge bases. The inference engine performs the process of inference from the facts and rules in the knowledge base. It is a basic principle of the architecture that the knowledge base and inference engine are separate.

The user interface has several functions. It is the means whereby the user supplies additional information to the system, either in response to demand or by volunteering it, and the means whereby he receives the output.

To these three basic features may be added a number of others. They include a blackboard, a knowledge acquisition facility, a learning facility and an explanation facility. A blackboard is a device for communicating with the knowledge bases and holding intermediate hypotheses and decisions. Only a proportion of systems incorporate a blackboard. A knowledge acquisition facility provides the means for the knowledge engineer to input knowledge elicited from the domain expert, allowing him to input and edit facts and rules, and so on. An inductive learning facility may also be provided. The user interface may contain an explanation facility.

30.24.5 Inference engine

The inference engine may incorporate any of a number of different inferencing, search and problem-solving methods. It may have forward or backward chaining, corresponding respectively to data- or goal-driven inference, or a mixture of both. It may use depth-first or breadth-first search, hill-climbing, means-ends analysis, generate-and-test, pattern-matching, and so on. Or it may use some hybrid scheme.

30.24.6 Blackboard

A blackboard is a device for holding a set of intermediate hypotheses and decisions, in other words partial solutions. It communicates with and draws knowledge from the set of knowledge bases in an opportunistic way. In some cases it can be regarded as being split into three parts: plan, agenda and solution. The plan part contains the goals, plans, states and contexts; the agenda the potential actions awaiting execution; and the solution the hypotheses and decisions. The blackboard can be altered only by the knowledge bases. Such forms of control as the blackboard has act to focus attention on a problem and the knowledge bases then indicate what contribution they can make.

30.24.7 Knowledge acquisition facility

It is helpful to the creation of an expert system if there is a knowledge acquisition facility (KAF) which provides for the editing of facts and rules and for their entry into the knowledge base.

There may also be provided a facility for inductive learning. This may be regarded as part of the knowledge acquisition facility or as a separate feature. In any event, the purpose of this facility is to allow knowledge to be entered in the form of a learning set of examples provided by the expert and rules to be induced from these examples. This is an alternative to the provision of explicit rules by the expert.

30.24.8 Explanation facility

Most expert systems are provided with an explanation facility which can provide some form of justification for the conclusion reached, but the sophistication of such facilities varies. Accounts of explanation facilities are given in *Expert Knowledge and Explanation* (Ellis, 1989) and by Sell (1985) and J. Martin and Oxman (1988).

There are two main types of user for an explanation facility, the knowledge engineer and the client user. There are several types of explanation which a user requires. One is elaboration of the questions which he is asked in order to assist him to answer them correctly. Another is justification for these questions in order to motivate him to provide answers to them. The third is an explanation of the reasoning process.

One of the simplest forms of explanation facility is rule-tracing. The system keeps track of the path by which it has reached the current point and can display this to the user on demand. A rule trace is relatively easy for the system to provide. A detailed example is given by Ellis (1989).

However, an explanation facility which utilizes a simple rule trace is somewhat crude. It is preferable that the line of reasoning be explained rather in terms of the principles which govern the domain, using domain knowledge in a structured way.

Considering the explanation facilities in actual expert systems, that used in MYCIN is effectively a rule trace. NEOMYCIN by W.J. Clancey and Letsinger (1981) utilizes a number of domain-specific meta-rules which control the problem-solving and is thus able to provide a more domain-related explanation.

The program XPLAIN by Swartout (1983) utilizes both a domain model, which is descriptive, and domain principles, which are prescriptive, and is able to provide an explanation which justifies rather than simply records the program behaviour.

In most cases the output of an explanation facility is confined to text. STEAMER by Hollan, Hutchings and Weitzman (1984), on the other hand, which deals with operations on a steam plant, provides both graphical and textual output.

Generally, an expert system is used by a quite small number of people. There tend to be considerable differences in individual preferences for output from an explanation facility. One way of accommodating this is to provide options which individual users can select.

In more advanced work on this topic, user models are utilized to improve the design of the explanation facility.

30.24.9 Building tools

There are available a number of tools for building expert systems. They include programming languages, expert system shells and expert system building environments. Accounts of building tools for expert systems are given in Hayes-Roth, Waterman and Lenat (1983) and J. Martin and Oxman (1988). Lists of some principal tools are given by Frost (1986) and Hu (1987).

The languages traditionally used for building expert systems are LISP and Prolog. Insofar as the early and classic systems were built in the USA where LISP was the favoured language, LISP has been predominant. Prolog implements logic programming. For object-oriented programming use may be made of SMALLTALK. Of the general purpose languages, C++ is particularly compatible.

An expert system shell is strictly a tool created from an existing expert system by removing the features which are specific to the original problem, whilst retaining the general structure and in particular the inference method. A tool of the same general type may be created from scratch, and is sometimes also referred to as a shell.

Shells are widely used and can be especially useful for prototyping. The weakness of shells is that problems vary in nature and a shell capable of dealing with a wide range of problems needs to be rather sophisticated. Thus

some applications require data-driven search, others require goal-driven search and others again require a mix. Some applications involve uncertainty, whilst others do not. Some applications may have large quantities of data but few rules, and others the converse. Lists of the principal shells are given by Frost (1986) and Hu (1987).

There are in addition a number of so-called 'environments' for the building of expert systems. These differ from shells in that they are more flexible. The concept of an expert system building environment is that it offers a wide range of features, particularly for the knowledge representation and the inference engine. Environments include KAS, OPS5 and AGE, described in the next section.

There are also numerous tools for particular individual features of expert systems. They include tools for building knowledge bases, knowledge acquisition facilities, learning facilities, the user interface, explanation facilities, and so on. There are knowledge base management systems, which fulfil functions somewhat similar to those of database management systems.

30.24.10 Knowledge elicitation and acquisition

Crucial activities in building an expert system are knowledge elicitation and knowledge acquisition. The two terms are often used almost interchangeably, but whereas in knowledge elicitation the emphasis is on eliciting the domain knowledge from the expert, in knowledge acquisition it is on providing the program with this knowledge. Accounts are given in *Knowledge Acquisition for Expert Systems* (Kidd, 1987) and *Knowledge Elicitation* (Diaper, 1989) and by Beerel (1987) and J. Martin and Oxman (1988).

The expertise of the domain expert has a number of facets. Typically, he has a wide experience and knowledge of case histories, problems, and solutions, both successful and failed. This background provides him with an understanding of the structure of the domain, of the crucial distinctions which have to be made, of the constraints which apply, of the problems to be solved, of the decompositions which can be made, of problem-solving and search strategies, of heuristics and rules-of-thumb, of facts and rules, and of exceptions and refinements.

The task of knowledge elicitation is generally undertaken by the knowledge engineer. His task is to acquire and represent the domain knowledge and to engineer the system so that it is easy for the user to utilize. The most common method of knowledge elicitation is interviewing of the expert by the knowledge engineer. The aim is to make explicit the expertize. There is a large literature on interviewing, especially in the social sciences. Another approach is close observation of the expert as he performs the task. Typically this utilizes some form of verbal protocol in which the expert explains what he is doing and why he is doing it. A third approach is for the expert to provide sets of problems and solutions and for the knowledge engineer to induce from these the internal rules which the expert is evidently using to obtain the solutions. A fourth method is prototyping, in which the expert and knowledge engineer co-operate to build a system. The expert furnishes knowledge for, and provides tests of, the system, while the knowledge engineer tries to create a suitable system structure.

The interaction between the knowledge engineer and the expert is not limited to debriefing the expert. They need also to work together to design the user interface. Decisions are required on the questions which he is to be asked and on the explanations which are to be provided for him.

The process of knowledge elicitation is generally incremental and iterative. The expert is unlikely to be able to make explicit his expertise in a particular area in a single pass, and the process of elicitation is likely to prompt him to make additions and refinements, or even to undertake a more fundamental restructuring.

The main domain expert is not the sole source of knowledge available to the knowledge engineer. He may also utilize the literature and databases, historical records, case histories and case studies, and interviews with other engineers. It should be borne in mind, however, that whereas the expertise of the single expert can reasonably be presumed to be coherent, an eclectic approach which draws on a wide range of sources is more likely to involve both inconsistencies and contradictions and out-of-date methods.

In some cases an expert system is created by the domain expert himself. In particular, it has become quite common for systems to be created utilizing an induction tool which is provided by the expert with a learning set of examples and solutions.

30.24.11 System evaluation

It is clearly necessary that at some stage an expert system should be evaluated, but such evaluation raises a number of issues which need to be addressed if it is to be done satisfactorily. The evaluation and validation of expert systems are discussed by Hayes-Roth, Waterman and Lenat (1983), Sell (1985), Beerel (1987) and Ellis (1989).

It is not self-evident that there is need for an evaluation of the system other than the ultimate test of successful use. In fact, however, there are benefits to be gained from evaluation prior to entry into service, both in terms of the quality of the system finally produced and of the learning process of the organization which is building the system.

Some issues which arise in the evaluation of an expert system are the criteria, the assessors, the timing, the methods and the overall evaluation process. An expert system generally captures the expertize of a single expert. A question therefore arises as to whether the system is to be judged by its success in reproducing that expertize or in solving problems. The distinction is a fundamental one. Another basic question to be decided is who is to perform the evaluation. The assessment may in principle be performed by the expert, the knowledge engineer and/or the client users. The timing of the evaluation is another issue, the options being to carry out interim assessments throughout the building of the system or to defer evaluation until it is complete. The methods used for the evaluation may be informal or formal ones.

Evaluation criteria which are based on the requirement that the system reproduce the expertise of the domain expert centre essentially on the ability of the system to provide high quality advice based on correct and acceptable reasoning. More specifically, criteria for the quality of the advice may relate to the following features:

(1) consistency, (2) completeness, (3) soundness, (4) precision and (5) usability. Consistency means that the system should give similar answers to similar questions. A small change should not induce totally different behaviour. Completeness implies that the coverage of the domain is comprehensive. The requirement for soundness is that the statements made are true. The precision requirement applies only where there are quantitative outputs, and has the usual meaning. Usability means here that the user interface should operate as intended, a requirement distinct from user-friendliness. The evaluation should address not only the quality of the conclusions but also the quality of the reasoning by which they are arrived at. This is not just a matter of correct inference, but has to do also with the extent to which particular conclusions are supported by an overall structure.

Criteria are also required to evaluate the discourse with the user. In large part these will centre round the questioning of the user and the provision of explanation to the user, which were discussed above.

An expert system is built with particular categories of user in mind, and ultimately it is they who must be satisfied. This does not necessarily mean that evaluation should be carried out solely by these users. Generally it will be appropriate for the knowledge engineer, the expert and the users all to be involved. The knowledge engineer is able to evaluate the program technically as an expert system, including here the user interface, whilst the expert can assess it in terms of the expert advice which is provides and the user in terms of the ease of use and value of the advice.

With regard to timing, it is preferable to conduct the evaluation as the building of the system progresses rather than to defer it to the end. User evaluation and feedback as the system is being created is a recurring theme in discussions of system evaluation.

The evaluation may be informal and qualitative or it may use formal and possibly quantitative methods. Some formal methods are described in Hayes-Roth, Waterman and Lenat (1983). Whatever other methods are used, two which are unavoidable are testing by the expert and use by the users. These tests may be informal but they should address the task which the system has been designed to perform and the criteria which have been agreed for its evaluation.

Evaluation of an expert system is not a straightforward matter. Sources of difficulty are: the potential confusion between defects in the system and in the expertise which it embodies; a lack of understanding by users of the scope and limitations of the system and unrealistic expectations for its performance; importation by users of extraneous criteria; disagreement about the relative importance of criteria; and deficiencies of the system whilst it is still only partially developed.

Accounts of case studies of the evaluation of expert systems are given in Hayes-Roth, Waterman and Lenat (1983). They describe assessment of the R1 system for computer system configuration and of the ORNL spill crisis management system, and the lessons learned about evaluation. Foremost among these lessons are the need to involve users early and fully. At the end of the day the ultimate test is whether the system is used, and, if so, whether it has proved cost-effective.

30.25 Expert Systems: Some Systems and Tools

30.25.1 DENDRAL

DENDRAL is an expert system which discovers molecular structures. Work on DENDRAL dates from 1965 and its creation was a landmark in AI. It is described by B.G. Buchanan, Sutherland and Feigenbaum (1969, 1970), B.G. Buchanan *et al.* (1976), B.G. Buchanan and Feigenbaum (1978) and Lindsay *et al.* (1980) and also by Hayes-Roth, Waterman and Lenat (1983), Winston (1984) and Patterson (1990).

The program determines the molecular structure of a substance from information on the constituent elements, or chemical formula, and the mass spectrograph. It has a structure enumerator, which synthesizes candidate chemical structures subject to constraints, derived largely from the mass spectrograph data, that certain structures must be present (the necessary list) and that certain structures must not (the forbidden list). For each candidate structure it synthesizes a mass spectrograph. It matches the synthesized spectrographs of the candidate structures to the experimental ones and selects the structure which gives the best fit.

The system is thus a problem-solving program which uses a generate and test strategy. The generation part involves a search which is partly guided by heuristic rules. It also contains other rule-based systems, one of which is a set of rules for structures in the forbidden list which supplement the mass spectrograph information. The test part is the spectrograph matching process.

The use of DENDRAL showed up some of the problems of knowledge elicitation. This led to the development of META-DENDRAL, which induces rules from examples (B.G. Buchanan and Feigenbaum, 1978).

30.25.2 MYCIN

MYCIN is an expert system for the diagnosis of infectious blood diseases. It is described in *Computer-Based Medical Consultation: MYCIN* (Shortliffe, 1976) and Rule-Based Expert Systems (B.G. Buchanan and Shortliffe, 1984) and also by Hayes-Roth, Waterman and Lenat (1983), Winston (1984), Charniak and McDermott (1985) and Patterson (1990).

The program is a rule-based production system. Initially it had some 200 rules which by the early 1980s had risen to about 600. A feature of the rules is the use of certainty theory. Each rule is assigned a certainty factor which is propagated through to yield a certainty for the result for each hypothesis. Search in MYCIN is a slightly modified form of depth-first search with backward chaining. The current hypothesis constitutes the goal of an AND/OR tree. MYCIN has an interactive facility. Backward chaining has the advantage over forward chaining that it is more compatible with user interaction. A search which proceeds by a process of elimination tends to generate a large number of questions, which is liable to irritate the user, and the interaction is modified so that the user is asked a smaller number of direct questions, the answers to which then guide the search.

Associated with MYCIN is TEIRESIAS, which was developed as a front end to aid knowledge acquisition. MYCIN has also given rise to EMCYIN, an expert system shell based on MYCIN.

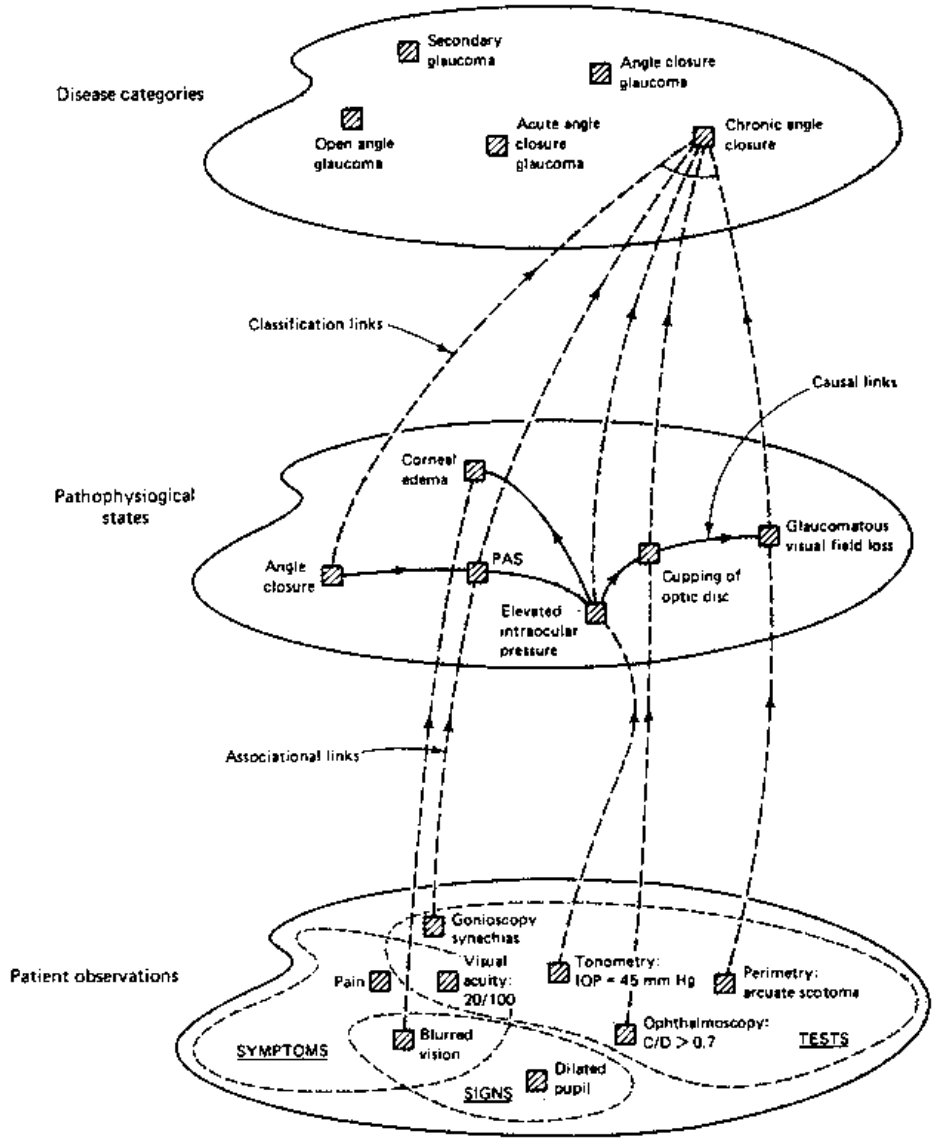


Figure 30.7 *Levels of knowledge in CASNET (Weiss et al., 1978) (Courtesy of North Holland Publishing Company)*

30.25.3 CASNET

CASNET is an expert system for the diagnosis and treatment of glaucoma, and is a research program. It is described by Weiss, Kulikowski and co-workers (Weiss, Kulikowski and Safir, 1977, 1978; Weiss *et al.*, 1978; Weiss and Kulikowski, 1981, 1983; Kulikowski and Weiss, 1982) and also by Hayes-Roth, Waterman and Lenat (1983) and Patterson (1990).

The program carries out diagnosis using three levels of knowledge: patient observations, pathological state and disease. Its general structure is shown in Figure 30.7. The use of the intermediate level of pathological state is a key feature of the approach taken in CASNET. CASNET utilizes an associative network or semantic net. Inference is effected by traversing the network in a search for the most plausible paths of cause and effect. The program also utilizes production rules.

30.25.4 PROSPECTOR

PROSPECTOR is an expert system which gives advice on mineral deposits. It is described by Duda *et al.* (1978), Hart, Duda and Einaudy (1978), Duda, Gaschnig

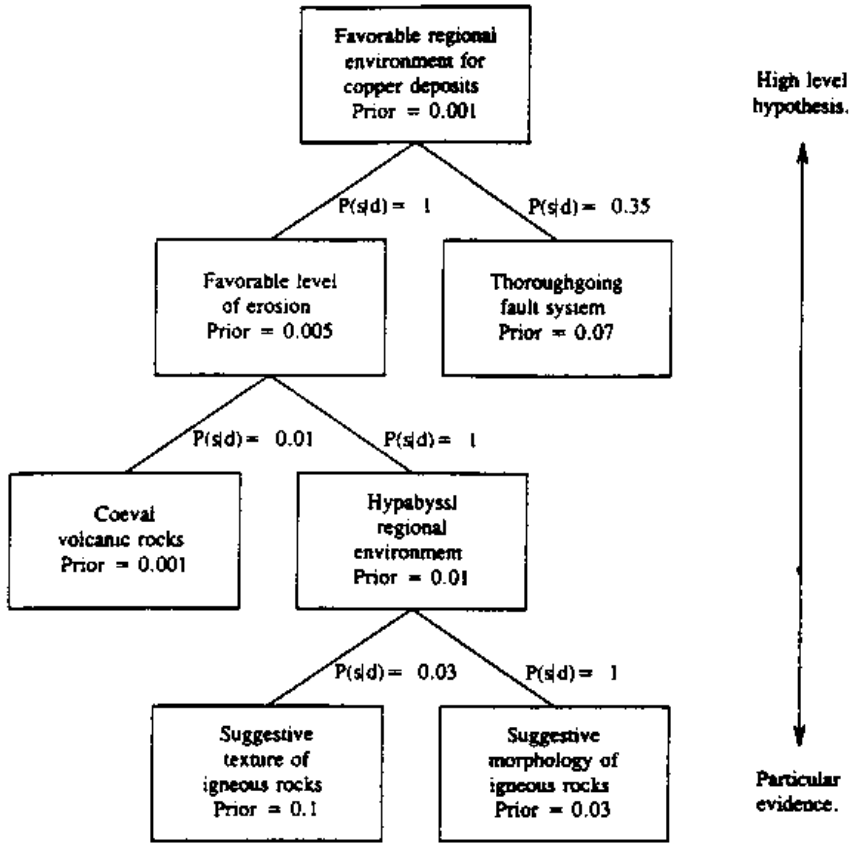


Figure 30.8 *Bayesian inference in PROSPECTOR (Charniak and McDermott, 1985) (Courtesy of Addison-Wesley Publishers)*

and Hart (1979) and A. Campbell *et al.* (1982) and also by Hayes-Roth, Waterman and Lenat (1983), Charniak and McDermott (1985) and Tanimoto (1990).

The program utilizes geological field data to advise on the likely locations of deposits of a particular mineral. Like CASNET, it makes use of an intermediate level of knowledge, and is one of the best examples of an expert system based on this feature. It contains 'models' of situations in which deposits of particular ores tend to occur.

PROSPECTOR is a rule-based production system. Explicit use is made of Bayesian inference, as shown in Figure 30.8. Where use is made of such Bayesian probabilities, it is necessary that the prior probabilities be consistent. Methods of approach to this problem are discussed by Tanimoto (1990).

The user has a facility to interact with PROSPECTOR. This includes the option to volunteer information.

30.25.5 CADUCEUS

CADUCEUS, originally called INTERNIST, is an expert system for the diagnosis of diseases of the internal organs, and is a research program. It is described by R.A. Miller, Pople and Myers (1982), Pople (1982) and also by Hayes-Roth, Waterman and Lenat (1983) and Charniak and McDermott (1985).

The authors of the program claim that it covers some two-thirds of the diseases of the internal organs. It deals with about 500 diseases in terms of some 3500 conditions. In addition to its wide coverage, another of its strengths is its ability to handle multiple diseases. The information used in the program includes not only symptoms but also medical history and laboratory test results. A feature of the search strategy used in CADUCEUS is that it involves a large bottom-up element.

Work on the development of CADUCEUS aims to make the program act more like a physician by making an initial global assessment, decomposing the problem and partitioning the symptoms among the separate subproblems.

30.25.6 R1/XCON

XCON, originally called R1, is an expert system for the configuration of VAX computer systems, and is in

industrial use. It is described by McDermott (1980, 1981, 1982a), and also by Hayes-Roth, Waterman and Lenat (1983), Winston (1984), Charniak and McDermott (1985) and Tanimoto (1990).

The program accepts an order for a computer system and performs the following aspects of system configuration: (1) check the order for missing and mismatched items, (2) create the layout of the processor in cabinets, (3) put boxes in the input/output cabinets and place components in these boxes, (4) put panels in the input/output cabinets, (5) create the floor plan layout, and (6) do the cabling. XCON is thus a problem-solving program. It is based on production rules.

The number of rules in XCON is large. In 1979 the program had about 800 rules, by 1983 about 3000 and by 1990 some 12000. The large number of rules requires an efficient search strategy. Search in XCON is by forward chaining. This search involves minimal backup. The rules apparently incorporate sufficient constraint that the search rarely goes up a blind alley. The method of inference in XCON is deductive. This distinguishes it from the diagnostic programs, where inference is by abduction. The program illustrates the fact that an expert system can be useful even if it is at a relatively early stage in its overall development. It was already in use in 1979.

XCON is of particular interest here for two reasons. It is the only one of the classic systems described which deals with design, and it is a system which has been in industrial use for well over a decade.

30.25.7 BAGGER

In addition to the classic expert systems just described, there are certain others which are also instructive. One of these is BAGGER, an expert system for bagging groceries in a supermarket., which is described by Winston (1984). Although essentially a toy system, BAGGER constitutes a useful introduction to an expert system based on production rules, including features such as conflict resolution.

30.25.8 EMYCIN

An early shell was EMYCIN (Empty MYCIN) (van Melle, 1979, 1980, 1981; van Melle, Shortliffe and Buchanan, 1981). It is a domain-independent system for the creation of expert systems for diagnosis or consultation. It retains the basic rule structure, inference engine and explanation facility of MYCIN. A further account is given in Hayes-Roth, Waterman and Lenat (1983).

30.25.9 Other shells

Other shells frequently mentioned are ESP ADVISER and SAVOIR. Some systems are variously referred to as shells or building tools.

30.25.10 ART

ART (Automated Reasoning Tool) was one of the first building tools. It is intended for use in building large systems and integrates a number of problem-solving techniques. ART is written in CommonLISP. An account is given by J. Martin and Oxman (1988).

30.25.11 AGE

Another early building tool was AGE (Nii and Aiello, 1979). AGE contains two types of entity: components and frameworks. A component is a routine which supports a basic AI mechanism and a framework a fixed configuration of components. A back-chaining framework and a blackboard framework are the two original frameworks. AGE is described by Hayes-Roth, Waterman and Lenat (1983).

30.25.12 KAS

KAS (Knowledge Acquisition System) (Duda, Gaschnig and Hart, 1979) is a knowledge acquisition system derived from PROSPECTOR. It places more emphasis than EMYCIN on information volunteered by the user, trying to avoid a large number of low pay-off questions and utilizing a mix of forward and backward chaining. Hayes-Roth, Waterman and Lenat (1983) give a further account.

30.25.13 OPS5

OPS5 (Official Production System 5) (Forgy, 1981) is one of the OPS family of building tools. It was developed as an aid in the building of R1/XCON. It may be described as a rule-based programming language and is used to build rule-based production systems which use, primarily, forward chaining. It incorporates the RETE algorithm. Accounts are given in Hayes-Roth, Waterman and Lenat (1983) and by Patterson (1990).

30.25.14 KEE

KEE (Knowledge Engineering Environment) is variously described as an expert system shell or building tool. It is has production rule, frame and object oriented system facilities. Inference is by inheritance and by forward and backward chaining. Accounts are given by Frost (1986) and Patterson (1990).

30.25.15 KES

Another system building tool is KES, which has production rule and frame facilities. An account is given by Frost (1986).

30.25.16 EXPERT

EXPERT (Weiss and Kulikowski, 1979, 1981) is a building tool for diagnosis- or classification-type consultation systems. An account is given in Hayes-Roth, Waterman and Lenat (1983).

30.25.17 EXPERTEASE and EXTRAN

EXTRAN, and the earlier EXPERTEASE, are classification tools based on the ID3 algorithm for inductive learning.

30.26 Qualitative Modelling

In engineering, the conventional method of modelling a physical situation to create a mathematical model consisting of algebraic and differential equations based on classical physics. In recent years there has been growing interest in an alternative approach which goes by the names of naive physics, and of qualitative modelling, qualitative physics, or qualitative simulation.

Accounts of naive physics and qualitative modelling are given in *Mental Models* (Gentner and Stevens, 1983), *Qualitative Reasoning about Physical Systems* (Bobrow, 1985), *Formal Theories of the Commonsense World* (Hobbs and Moore, 1985), *Readings in Qualitative Reasoning*

about Physical Systems (Weld and de Kleer, 1990) and *Recent Advances in Qualitative Physics* (Faltings and Struss, 1991) and by Forbus (1984), de Kleer and Brown (1984), Kuipers (1984), Hardt (1992) and de Kleer (1992).

30.26.1 Naive physics

Classical physics is based on qualitative concepts which are then translated into quantitative mathematical models. Naive physics utilizes the same concepts but derives from them qualitative models. Work on naive physics has been described by Hayes (1979, 1985) and Hardt (1992). The work on qualitative modelling by de Kleer and Brown (1984), Forbus (1984) and Kuipers (1984) also comes under this head.

In naive physics the physical situation is modelled formally but qualitatively. The modelling remains symbolic and the variables take a limited number of discrete states. Naive physics retains all the basic concepts of classical physics such as state, equilibrium, conservation of mass, momentum and energy, and so on, but treats them in a qualitative way. It follows the same sequence of model formulation, solution and interpretation of the results.

One way of looking at naive physics is that it is a formal encoding of common sense reasoning about physical situations. In many cases, particularly in mundane situations, it can be quite difficult to formulate a quantitative mathematical model, but it is feasible to derive a qualitative model. In its own terms the qualitative model can be made as rigorous as the quantitative one.

A naive physics model can also be viewed from the opposite perspective as a reduction of a quantitative model to its essential qualitative form. In some work on naive physics models have been derived both by encoding of natural language statements and by reduction of the equations of a conventional mathematical model to qualitative model format.

The formalization of common sense reasoning about physical situations in a naive physics model is not easy. Common sense draws on large quantities of knowledge about the physical world and the forms of knowledge representation involved are often specialized.

The approach advocated by Hayes (1979) in his 'naive physics manifesto' is the use of predicate calculus. In fact, the three main developments in qualitative modelling have not adopted this approach. These developments are component-based modelling, constraint-based modelling and process-based modelling.

30.26.2 Fault propagation

As it happens, some of the early work on qualitative modelling was in the process field. Qualitative models were used by Andow and Lees (Andow, 1973; Andow and Lees, 1975) to model fault propagation in process plants. The purpose of the work was to determine the interaction between process variables with a view to creating alarm trees for alarm diagnosis by process computer.

The basic principle may be illustrated by considering the differential equation for the change in level in an open tank with water flowing in and out:

$$\frac{dL}{dt} = Q_1 - Q_2 \qquad [30.26.1]$$

where L is the level, Q is the flow and t is time, and subscripts 1 and 2 denote the inlet and outlet, respectively.

In the work of Andow and Lees the equations of the corresponding qualitative model were obtained from those of a conventional mathematical model. Thus the qualitative model equation equivalent to Equation 30.26.1 is

$$L = (+Q_1, -Q_2) \qquad [30.26.2]$$

which signifies that L increases if Q_1 increases or Q_2 decreases, or vice versa.

It may be noted that Equation 30.26.2 may also be obtained by encoding an engineer's natural language statement that 'The level increases if the flow in increases or the flow out decreases, and vice versa'. It constitutes, in effect, a half-way house between a description in natural language and that of a quantitative model.

Work on fault propagation is described in Section 30.36.

30.26.3 Qualitative modelling

As stated above, qualitative modelling has developed in three main directions. These are: component-based, or device-based, modelling, as in the work of de Kleer and Brown (de Kleer, 1975, 1985; J.S. Brown and de Kleer, 1981; de Kleer and Brown, 1983, 1984, 1986); process-based modelling, as in the work of of Forbus (1983, 1984, 1990); and constraint-based modelling, as in the work of Kuipers (1984, 1986). Of these three methods, component-based modelling appears the most suitable for the qualitative modelling of process plant and it is therefore this which is primarily considered here, but a brief account of the other two methods is appropriate.

30.26.4 Process-based modelling

In the process-based modelling of Forbus (1984), the physical situation is described in terms of the physical process which over time cause changes to occur. The physical processes are those such as flowing, heating, cooling, boiling, and so on.

30.26.5 Constraint-based modelling

In the constraint-based modelling of Kuipers (1984, 1986), the physical situation is described in terms of the variables and the constraints relating these variables. Three principal types of constraint are used. These are:

Arithmetic: $X = Y + Z$
Functional: $Y = M^{+}(X)$
Derivative: $Y = dX/dt$

The arithmetic constraint requires that the values of the variables have the indicated relationship at all times; the functional constraint requires that Y is a strictly increasing function of X (or, for M^{-}, a decreasing function); and the derivative constraint requires that Y is the rate of change of X. Thus the constraints consist of a qualitative adder, a qualitative proportionality and a qualitative differential.

30.26.6 Component-based modelling

The component-based modelling approach of de Kleer and Brown (J.S. Brown and de Kleer, 1981; de Kleer, 1984, 1992; de Kleer and Brown, 1984) involves decomposing the system into separate, context-independent entities which are then modelled. These entitities are materials, components and conduits. Examples of materials are fluids or current; examples of conduits are pipes or wires.

A component-based approach is well suited to the modelling of systems with a fixed topology such as items in a process plant. The approach is essentially reductionist. An overview of component-based modelling has been given by de Kleer (1992) and the account here draws on this.

30.26.7 Composability

It is a basic principle of qualitative modelling that the model of a component should be independent of the context. This is the 'no-function-in-structure' principle. De Kleer illustrates this principle with the example of an electric light switch. A model of the switch which makes the unqualified statement 'If the switch is off, no current flows; and if the switch is on, current flows' violates the principle. Situations can be envisaged, such as that where there is another switch in series, where it might not be true. The correct formulation is that current flows if the switch is on and there is potential for current flow.

30.26.8 Quantity spaces and landmarks

In the notation for qualitative modelling used by de Kleer a qualitative value of x is denoted by $[x]$. The qualitative value of x is defined in relation to some reference, or landmark, value. A basic quantity space is the +, −, 0 value space. This means that $[x] = +$ if $x > 0$; $[x] = -$ if $x < 0$ and $[x] = 0$ if $x = 0$.

The landmark value may be taken not as zero but as some other value, say a. In this case the origin is shifted by defining some new variable, say y, as $y = x - a$.

Basic issues in qualitative modelling are the choice of the quantity space and of the landmarks.

30.26.9 Qualitative equations and arithmetic

Basic arithmetic operations in qualitative modelling are addition

$$[z] = [x] + [y] \qquad [30.26.3]$$

and multiplication

$$[z] = [xy] = [x][y] \qquad [30.26.4]$$

In these relations, the qualitative value of $[z]$ is fully defined for multiplication, but for addition it is indeterminate. The relationships for addition and multiplication in qualitative arithmetic are shown in Table 30.4.

For derivatives, the notation

$$\left[\frac{dx}{dt}\right] = +$$

signifies that x is increasing. An alternative notation for $[dx/dt]$ is ∂x.

It is not permissible to manipulate qualitative equations according to the same rules as conventional ones. In particular, an operation such as the subtraction of $[y] + [z]$ from $[x] + [y] + [z] = 0$ does not necessarily yield $[x] = 0$.

Table 30.4 *Some relationships of qualitative arithmetic*

A Addition [x] + [y]

[y]	[x]		
	−	0	+
−	−	−	?
0	−	0	+
+	?	+	+

B Multiplication [x][y]

[y]	[x]		
	−	0	+
−	+	0	−
0	0	0	0
+	−	0	+

In the qualitative modelling method of de Kleer, an expression in terms of qualitive values, operators and variables is referred to as a confluence. A typical confluence used by this author is

$$\partial P + [P]\partial A - \partial Q = 0 \qquad [30.26.5]$$

where A is the area of an open control valve, P is the pressure drop across the valve and Q is the flow though it.

A set of qualitative values satisfies a confluence either if the qualitative equality strictly holds in accordance with the relations given in Table 30.4 or if one side of the confluence remains indeterminate because the addition operation is not closed. A set of values contradicts a confluence if both sides evaluate to a distinct qualitative value and the confluence is not satisfied. These statements imply that a confluence may be neither satisfied nor contradicted if some of the variables do not have assigned values.

Confluences are not used in the qualitative modelling work of Forbus or Kuipers.

30.26.10 Qualitative models

A component may have a number of states, each associated with a particular regime. A model of a component for the full set of regimes is termed a state specification.

Such a model may be illustrated by the valve model given by de Kleer (1992). This is

$[A = A_{max}];\ [P] = 0;\ \partial P = 0$ Valve open

$[0 < A < A_{max}];\ [P] = [Q];$ Valve working

$\partial P + [P]\partial A - \partial Q = 0$

$[A = 0];\ [Q] = 0;\ \partial Q = 0$ Valve closed

where the subscript max denotes the maximum.

An account has been given by de Kleer of the treatment of flow-like and pressure-like variables in component modelling. For flow it is assumed that the fluid is incompressible and the conduit runs full, and the principle of conservation of mass is applied. This rule is termed the continuity condition. For pressure it is

assumed that the sum of the pressure drops in the conduit is constant. This rule is the compatibility condition.

30.26.11 Time effects

Qualitative modelling is concerned with changes, and changes take place over time. The modelling must therefore take time into account in some way. It is not unusual in qualitative modelling work for the time aspect to be somewhat fuzzy. This is commonly so in fault tree studies, as already described.

There are three main methods which have been used for modelling change over time: the use of a sequence of intervals (Forbus, 1984); the use of intervals separated by a number of instants (de Kleer and Brown, 1984); and the use of intervals separated by single instants (Kuipers, 1984).

Rules necessary for reasoning about change over time have been derived by B.C. Williams (1984a,b) and are described by de Kleer (1992).

30.26.12 Dependence and causality

De Kleer draws a distinction between dependence and causality. It does not follow that because one variable is dependent on another, it is necessarily caused by it. For causality to apply, stricter criteria must be met. Two such criteria are locality and temporal order. Locality requires that for one variable to be a cause of another, the two variables must describe the behaviours of components which are physically adjacent, and temporal ordering requires that for one variable to be the cause of another it must precede it, even if only by an infinitesimally short interval of time, or mythical time.

30.26.13 Ambiguities and multiple interpretations

As already indicated, qualitative modelling is inherently ambiguous, and thus gives rise to multiple behaviour predictions, or interpretations. How serious this is for modelling in a particular application depends largely on the extent to which it is possible to devise rules for the elimination of some of the interpretations.

30.26.14 Envisioning

The reasoning process which uses qualitative modelling to produce a description of the behaviours of the system over time is termed envisioning. An illustration of envisioning is given by de Kleer (1992). He presents a stage–by–stage account of the behaviour of a mass-spring-friction system and shows that qualitative modelling can be used to envision the oscillatory behaviour of the system.

30.27 Engineering Design

Applications of AI have been mainly in the fields already described, but there is an increasing amount of work in engineering. The material of prime interest here is that on process plant design, which is described below, but first some consideration is given to design expertise and to AI applications in engineering design generally.

30.27.1 Design expertise

Accounts of the design process in general include *Introduction to Design* (Asimow, 1962), *The Nature of Design* (Pye, 1964), *Design Engineering* (Dixon, 1966), *An Introduction to Engineering and Engineering Design* (Krick, 1969), *Engineering Design* (Middendorf, 1969), *Management of Engineering Design* (Leech, 1972), *Supplementary Readings in Engineering Design* (Geiger, 1975), *A Students Introduction to Engineering Design* (Simon, 1975) and *The Sciences of the Artificial* (Simon, 1969).

The design process and expertise in design are somewhat elusive. Designers have found it difficult to explain their skill and others who have studied it have also found it hard to pin down. Broadly, however, the design process involves problem recognition and definition, problem decomposition, the generation of alternative options and selection from these options.

The expert possesses a knowledge base in which knowledge may be represented in a number of forms, many being analogous to those described earlier. He has available a mental library of design archetypes. He has knowledge relevant to the evaluation of situations such as: the frequency, or probability of events; the consequences of events; and the costs, in money and other factors. He is aware of constraining factors such as project objectives; costs; time; hazards; regulatory requirements; standards and codes requirements; and so on. He is able to make distinctions of all sorts which would probably not occur to the layman. He possesses the ability to decompose a problem into subproblems which have only weak interactions and which are more manageable. He has methods of working which include logical argument, rules-of-thumb, mental models, and analogues.

Part of the skill in engineering design consists of a knowledge of design methods for specific situations and equipment, based usually on appropriate mathematical models. This is the type of expertise with which the young engineer fresh from college may be expected to be familiar. Another part of the expertise comprises a personal collection of rules, many of them not explicit. These include both rules-of-thumb and heuristics, which guide the search for solutions. In this type of expertise the experienced engineer may be expected to have the advantage.

With design in general it is the initial conceptual stage which is the most critical. Closely related to this is the concept of design based not on trial and error but in getting it right first time.

30.27.2 Expert systems

The application of AI to engineering design is still in its infancy. A principal trend, however, has been the use of expert systems. An influential application of expert systems to engineering design was R1, or XCON, which has already been described in Section 30.25. Another application of AI quite common in engineering design is the use of classification systems.

30.27.3 Design architectures

There are, however, developments which start from a critique of these current approaches. One such is described in *Design Problem Solving* by D.C. Brown and Chandrasekaran (1989). The stance taken by these authors is broadly as follows. Most applications of AI in engineering design take the form of expert systems. These tend to be general expert systems, often shells, which use domain-independent control and inference, and

are simply loaded with the rules and data for the particular problem. They argue that typical practice with programming languages, system building tools and shells tends to involve the use of particular control structures even though this may not be apparent. They state:

> The fact that the low level language is used to implement a higher level control structure results in the knowledge base actually containing quite a few rules that are really programming devices for expressing this higher level of control. That is, the much talked about separation of knowledge from inference is not really true in practice for complex problems.

It is argued by Brown and Chandrasekaran that for efficient design it is necessary to take account of the specific domain and that there are generic tasks characteristic of each domain. Whilst there may be a range of features which are common to tasks in any domain of engineering, the relative importance of these features varies so greatly that it is not effective to adopt a uniform approach. Excessive emphasis on domain-independence suppresses the distinctions in control and inference which are characteristic of human conduct of generic tasks in different engineering design domains.

The framework for design which they propose is one which accommodates the domain-specific features. Design is viewed as the use of a number of different, and co-operating, types of problem-solver. The basic design process is that of generate and test. Four strategies are described for generating, or proposing, designs; (1) design decomposition, (2) design plans, (3) design by critique and modification of nearly correct designs, and (4) design by constraint processes.

The first approach involves decomposing the design problem into suitable sub-problems and creating a design hierarchy. Features of this process are the conversion of the goals and constraints of the overall problem into goals and constraints on the subproblems.

The design plans are pre-compiled partial design solutions. A design plan contains a sequence of design actions. Strategies for the retrieval of such plans include attachment of plans to goals or to components. NOAH may be viewed as a program which instantiates and expands design plans, since for each goal of the item under design, there is a stored procedure, effectively a plan.

Another way to proceed is by critique and modification of almost correct designs. This is applicable where such almost correct designs can be retrieved and converted to correct designs by processes of matching, critique and modification. Modification may involve the use of a number of problem-solving methods which may include means–ends analysis, hill-climbing and dependency-directed backtracking.

The fourth approach is design by constraint processes. This is applicable where there is a structure but the parameters are still to be determined. It proceeds by propagation of the constraints and incremental convergence on a solution which satisfies them all.

The authors distinguish three classes of design. Class 1 is creative design, essentially innovation and invention. Class 2 typically involves powerful decomposition and complex failure recovery features. Class 3 is routine design in which the problem is readily decomposable with only weak interactions between the subproblems and which is characterized by routine plans and failure recovery mechanisms.

30.27.4 DSPL

Brown and Chandrasekaran describe an expert system architecture for a Class 3 design and the programming language DSPL (Design Specialists and Plans Language) created to perform such design. DSPL contains design agents in the form of specialists, plans, tasks, and steps. There is a hierarchy of specialists each of which possesses a set of plans and has the function of plan selection. A plan is a sequence of calls to specialists or tasks. Each plan has a sponsor which matches the characteristics of the plan with those of the task for which it is a candidate. A task is a sequence of steps which it executes. The primitive design agent is the step. It provides a value for an attribute of the design.

A feature of DSPL is the failure handling. The basic approach taken is that the design agent concerned detects, diagnoses and fixes its own local failures and passes on only those failures which it cannot correct.

The authors give a detailed account of DSPL covering, in addition to the architecture features just mentioned, the handling of the database, constraints, dependencies and problem-solving. They describe DSPL itself and given an example of the design of an air cylinder system.

30.28 Process Applications

Turning now to the use of AI, expert system and other advanced techniques in the process industries, a number of overviews have been published. They include those of Stephanopoulos and Townsend (1986), Westerberg (1989), Hutton, Ponton and Waters (1990) and Stephanopoulos (1990).

The following areas of application can be identified:

(1) project aids –
  (a) aids for handling issues,
  (b) aids for handling requirements:
(2) process synthesis –
  (a) reaction route,
  (b) energy;
(3) plant design: synthesis –
  (a) inherently safer design,
  (b) classification activities,
  (c) designs with shallow structure,
  (d) designs with deep structure;
(4) plant design: analysis –
  (a) hazop,
  (b) fault tree analysis;
(5) operating procedures;
(6) process monitoring;
(7) fault administration;
(8) malfunction detection.

These various computer aids fall into four broad categories, as aids for (1) the design project, (2) the design synthesis, (3) the design analysis and (4) the plant operation. Thus item (1) in the above list covers aids for the design project as a whole, items (2) and (3) cover the process and plant design synthesis aids, item (4) covers plant analysis aids, and items (5)–(8) plant operations aids.

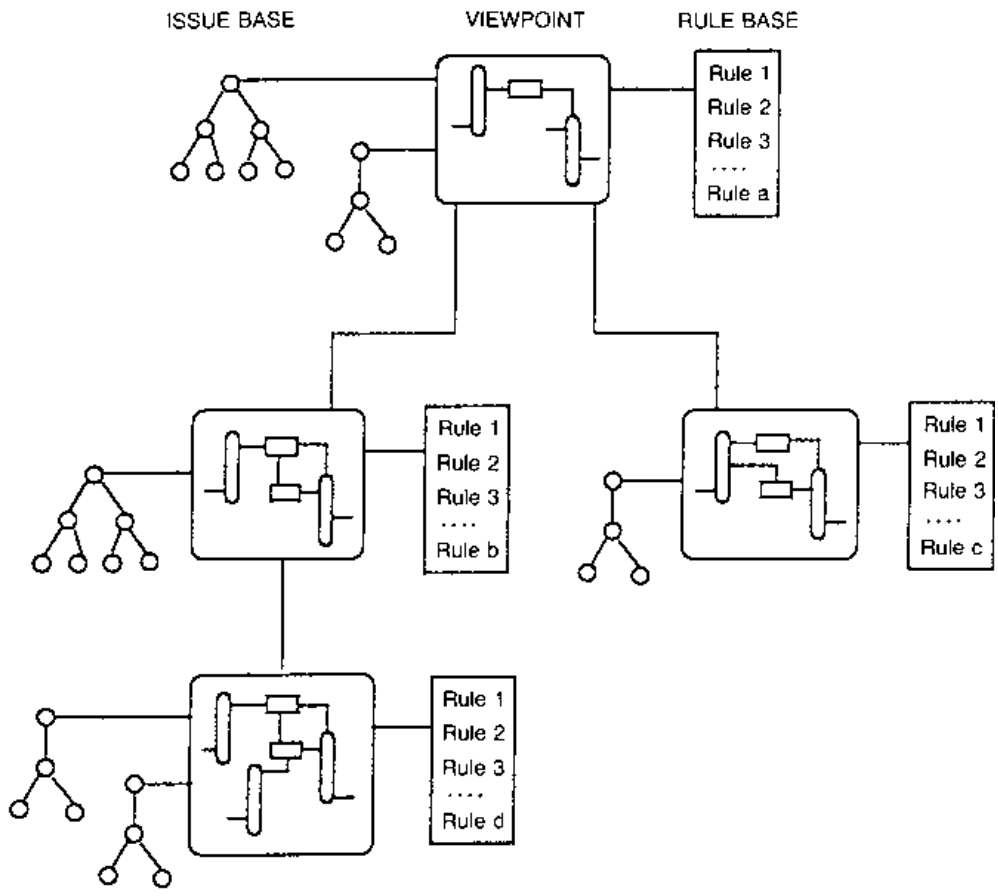


Figure 30.9 *Aid for the representation of design issues and history: system overview (Chung and Goodwin, 1994) (Courtesy of Kluwer Academic Publishers)*

Computer aids for process and plant synthesis may be termed front-end aids, whilst aids for plant analysis are back-end aids. Another way of looking at the matter is in terms of the generate-and-test concept: the synthesis aids represent the generate phase and the analysis aids the test phase. These various aids are considered in the sections which now follow.

30.29 Project Aids

It is appropriate to begin the account of AI aids for process plant design by considering those which address design problems at the highest level.

30.29.1 Aids for representing design issues and history

Design involves the identification of a succession of issues, discussion of these issues and decisions to select particular options. There are a number of benefits to be had by adopting a more formal approach to the handling of design issues. Such an approach imparts greater structure to the decision-making process, assists communication and co-operation between the different design disciplines and provides a record of design information. This information is of various kinds and includes the design intent, the chronological development of the design, the issues raised, the constraints recognized, the rules applied and the decisions made.

This record is of particular value when a design is undertaken which draws on that for an existing plant. Unless such information can be retrieved, the designers of the new plant may be unaware of significant issues and constraints and may not appreciate the reasons for certain design features. In the more serious cases, some assumption or feature critical to safety is not appreciated.

Parties concerned with the design can see the issues under discussion and can make their contribution by raising further issues, proposing alternative solutions, advancing further arguments for or against a solution and drawing attention to facts relevant to, or making comments on, an argument. Needless to say, if a decision aid is used in this way there needs to be a policy governing the parties authorized to access it and to modify it.

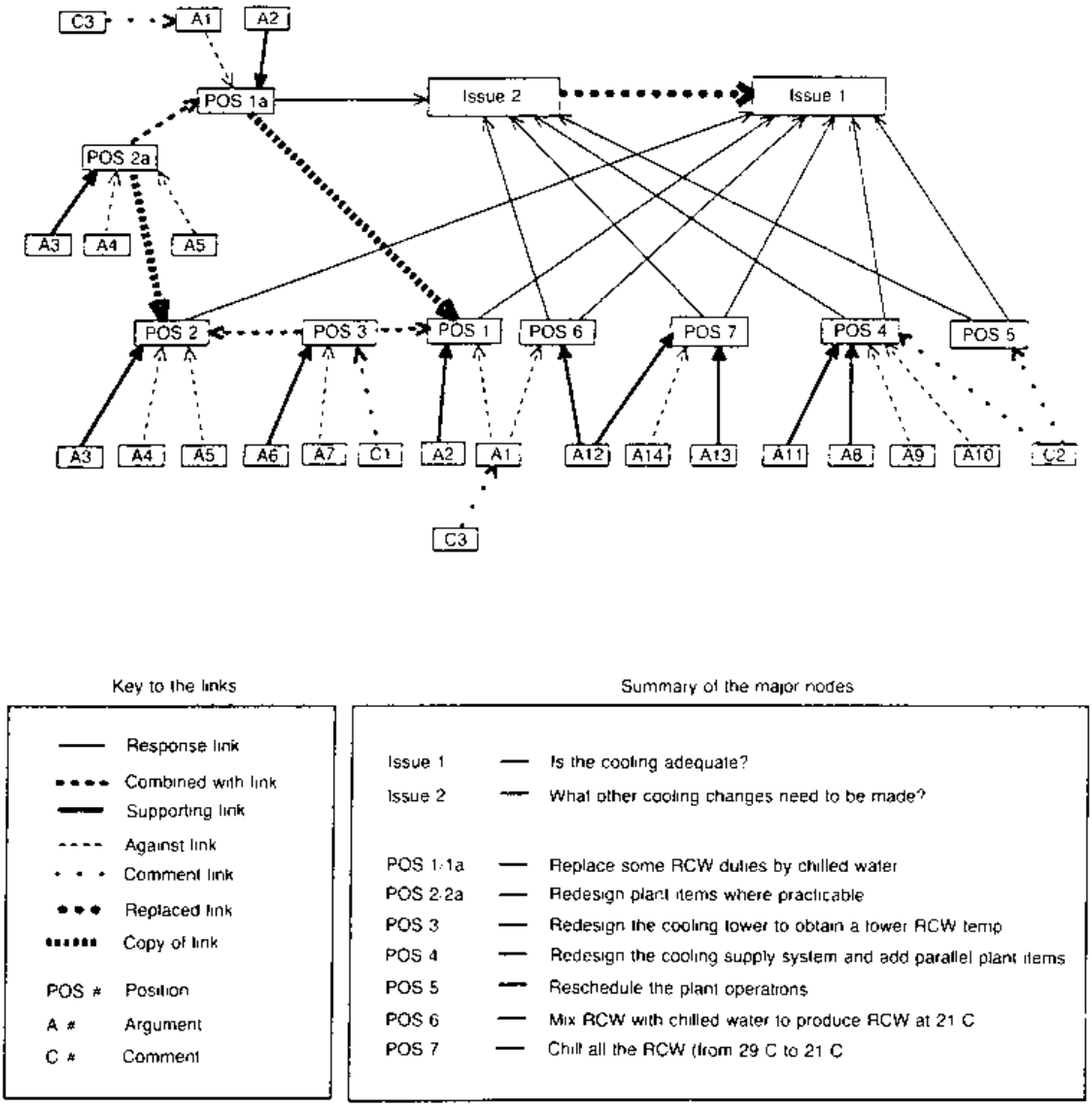


Figure 30.10 *Aid for the representation of design issues and history: issue base for the decision on the selection of cooling water temperature. RCW, recycled cooling water (Chung and Goodwin, 1994) (Courtesy of Kluwer Academic Publishers)*

Work on this topic, and on the creation of associated computer aids, has been described by a number of workers including Kunz and Rittle (1970), Conklin and Begeman (1988), Potts and Bruns (1988), Ganeshan, Finger and Garrett (1991), Lubers (1991), Chung, Abbas and Robertson (1993), Ramirez-Dominguez and Banares-Alcantara (1993) and Chung and Goodwin (1994).

An intelligent information system for safe plant design is described by Chung and Goodwin (1994). An overview of the system is shown in Figure 30.9. The system is issue-based, allowing the issues arising in the design and the arguments related to the issues to be represented and captured. It provides a historical record of the development of the design and of the issues affecting this development. Elements of the system are (1) the viewpoint mechanism, (2) the issue base and (3) the rule base.

The viewpoint mechanism is used to represent the design hierarchy. Each viewpoint is a single point in the design space. The viewpoint hierarchy provides a

chronological record of the states of the design. The viewpoint mechanism allows the designer to move around the design from node to node whilst maintaining consistency. A record is kept of the design changes and of the constraints and rules together with a list of previous viewpoints. When the designer changes viewpoint the mechanism traces back from the root to that point, reasserting all the constraints, rules and decisions stored along the way. The viewpoint mechanism also ensures that all changes made to one node are propagated through the design from the parent node to the child nodes.

The core of the system is the issue base. This provides a record of the issues considered. An issue is identified, positions are taken and arguments adduced for or against each position. In due course a decision is made to select one of the positions, or options.

Figure 30.10 shows an issue base for the following case:

> A chemical company wants to build a new plant in the USA. There is an existing plant for the same tonnage and product in the UK which uses both recycled cooling water (RCW) at 21°C and chilled water at 5°C. There are heavy demands on the cooling. The atmospheric ambient and wet bulb temperatures are higher at the proposed US site by 5°C and 8°C, respectively, on average. Are any modifications needed to the plant items and/or cooling supply systems?

The structure consists of nodes and semantic links. As shown, an argument is linked to a position by a *support* or an *against* link and a position is linked to an issue by a response-to link.

The authors also describe other types of node and link found necessary in developing this basic structure. Additional types of node used are *fact, comment* and *decision* nodes and additional types of link are *follow-up, combined-with* and *replaced-by* links. The first of these links allows re-examination of an issue on which a decision has already been made, the second allows the combination of several positions to form a single response and the third decomposition of the problem into a set of smaller ones. These extensions thus cater for features such as iteration and decomposition, which are characteristic of design.

The rule base constitutes the third main element of the system. This contains both general rules and rules specific to the particular design.

30.29.2 Aids for representing regulatory and code requirements

Another generic problem in design is the handling of the requirements of legislation, standards and codes, and company policies. The number of documents containing requirements and the number of individual requirements is generally very large, and this poses a major information handling problem. An account of the development of the aids to assist with such information handling has been given by Chung and Stone (1994). The problem has several different aspects, including the retrieval of the requirements relevant to a particular issue and the comprehension of these requirements.

Considering first an individual document such as a standard, three distinct approaches to the problem may be identified. The first is to accept the document as it is and provide aids to the user in finding his way around it. The second is to perform some kind of processing on the document. The third, and most radical, is to intervene at the stage when the document is being written and provide aids to assist the author in writing it.

The retrieval problem has two aspects: retrieval of whole documents and retrieval of requirements from within a document. For both types of retrieval widespread use is made of keywords. For retrieval of whole documents these may be words in the title, keywords provided by the author or keywords searched in the text. The use of combinations of keywords narrows the search space.

Bourdeau (1991) has described the creation of a major keyword-based system REEF which is a 15 000 page encyclopaedia consisting of about 1000 documents commonly used by French building professionals. The database contains about 75% text with the rest made up of some 3500 tables, 9000 drawings and numerous formulae. Information is indexed at two levels, that of the document and that of the information unit.

Another approach is to analyse the hierarchy of concepts in a document and to provide an aid based on search down through the hierarchy.

Another aid to retrieval is hypertext. This allows the user to browse through a document looking at related items. This too is based on some form of hierarchy or network of relationships.

Further progress is likely to depend on a more fundamental approach. Work in this area has developed in the direction of the modelling of the knowledge domain. This work bears both on retrieval and on comprehension. There are a number of methods which deal with relationships. Relationships between objects in a hierarchy and attributes of objects may be represented in a type hierarchy and the constituent parts of an object in a part hierarchy. Dependencies may be represented in network form. For the conclusion of a conditional statement, the pre-conditions may be shown in order of precedence in an ingredience network. A complementary representation is a dependence network which shows all the conclusions to which a given condition contributes. Requirements can be converted to various logical forms. These include logic programming, production rules, decision tables and so on.

One outcome of this sort of approach is the conversion of the document into an expert system. As can be imagined, this is a major task. Nevertheless, several expert systems of this type have been created, mainly in the building field.

The use of methods such as logic programming or production rules raises a number of issues such as the mixing of domain and control information and the updating of the program when requirements are changed, which are discussed by Chung and Stone. One approach being taken to overcome such problems is the development of generic standards processors, which allow the user to input the domain information in a purely declarative way. Another development is automated text formalization, which is essentially the application of natural language comprehension methods such as parsing to convert the text into formal language. A more radical departure is the development of author support systems to ensure that the original document is written in a more structured and formal manner. This

addresses at source the defects which later lead to problems of retrieval and comprehension.

In the account given so far, consideration has been limited to a single document. There is also the problem of retrieving, comprehending and reconciling requirements from a variety of bodies. A limited amount of work has been done by researchers on author support systems, such as the work by Stone and Tweed (1991) on the capture of information from the common sources on which regulations, standards and codes draw.

Aids for handling the requirements which a design must meet are potentially invaluable, but it will be apparent from the foregoing that their development is in its early stages.

30.30 Process Modelling

Before considering process and plant design as such, it is necessary at this point to say something about modelling. It has become clear from attempts to apply AI to a number of problems in this area that a common lesson is the need for modelling of the process and the plant. Such models are often referred to as deep level knowledge in contrast to compiled knowledge such as rules. Some areas in which modelling is required are process and plant design, planning of plant operations, and the diagnosis of faults on operating plant.

Such modelling draws particularly on the fundamental work on qualitative modelling described in Section 30.26, and especially on that of Kuipers and of Forbus on componented qualitative modelling and qualitative process theory, respectively. Some principal developments in qualitative modelling are now described.

30.30.1 Modelling languages and environments

Methods based on qualitative modelling tend to require the availability of a considerable number of models. The manual configuration of models requires considerable effort and can be a limiting factor in the use of the methods.

There have been a number of approaches aimed at mitigating this problem. One is the development of modelling languages such as OMOLA (Andersson, 1989; Nilsson, 1989), MODEL.LA (Stephanopoulos, Hanning and Leone, 1990a,b) and ASCEND (Piela *et al.*, 1991). Another development is automatic model generation.

The characteristic approach is the identification of common features of models and of a hierarchy of models with inheritance of features.

30.30.2 MODEL.LA

MODEL.LA is a modelling language for the interaction or automatic construction of models of process systems. It is designed to be able to generate models at various levels of abstraction, to capture qualitative, semi-quantitative and quantitative knowledge, and to produce complete documentation of the modelling context such as the process task and the assumptions and simplifications.

It has an object oriented structure. The syntax is described as an extended Backus–Naur form. It utilizes six modelling elements: generic unit, port, stream, modelling scope, constraint and generic variable. There are 11 semantic relationships obeying basic axioms of transitivity, monotonicity, commutativity and merging. The structure of the models is depicted by digraphs which are constructed by algorithms driven by the modelling context.

30.30.3 Model generation

Closely related to the use of modelling languages is the systematic, and hence automatic, generation of models. Work on this topic has been described by Catino, Grantham and Ungar (1991). These authors' work utilizes Forbus' qualitative process theory (QPT). The approach taken is based not so much on process units such as reactors and heat exchangers as on process phenomena such as reactions and heat exchange. The authors describe the use of an adaptation of QPT to configure such models, and the creation of a prototype model library.

30.30.4 Order-of-magnitude modelling

A methodology for formal order-of-magnitude, or O(M), reasoning in process engineering has been outlined by Mavrovouniotis and Stephanopoulos (1988). In qualitative modelling use is made of qualitative values (−, 0, +). For some purposes, this treatment of the quantity space is not sufficiently expressive. It is desirable to be able to have a more adequate treatment of absolute and relative values and to be able to take into account concepts such as 'much smaller than' or 'slightly larger than'. The O(M) method provides a means of doing this.

30.30.5 Dynamic qualitative modelling

Most work in qualitative modelling is confined to the steady state, but there is some work emerging on unsteady-state, or dynamic, qualitative modelling. Thus a method for the dynamic qualitative modelling and simulation of process systems is described by Dalle Molle, Kuipers and Edgar (1988).

30.30.6 Mathematical programming

Another area of modelling is mathematical programming, specifically mixed integer linear programming (MILP) and mixed integer non-linear programming (MINLP). An account of the relationship between MILP and logical inference for process synthesis is given by Raman and Grossman (1991), who show that qualitative knowledge on process synthesis which can be expressed in propositional logic form can also be represented in the form of equivalent linear equations and inequalities.

30.31 DESIGN-KIT

A number of computer aids for design such as building tools and environments have been created. One of these is DESIGN-KIT described by Stephanopoulos *et al.* (1987). DESIGN-KIT is a process design environment built on CommonLISP and KEE. It is intended in the first instance to support the synthesis of process flowsheets, the configuration of control loops for complete plants, the planning and scheduling of plant-wide operations and the operational analysis of plants.

The underlying philosophy is that the designer should have available an environment which allows him to move consistently between the tasks of: (1) the conceptual design of processing schemes and the evaluation of alternative chemistries, and mass and energy balances; (2) the simulation and evaluation of designs in respect of

Table 30.5 *Some features of DESIGN-KIT (after Stephanopoulos et al. , 1987)*

1.	Generation of graphic descriptions, e.g. flowsheets, control structures, material and energy balances, operational paths, etc., with windowing facilities and menu-driven operations
2.	Automatic generation of data structures describing the graphic objects
3.	Modular construction of new graphic objects, process units models, design methodologies, operational objectives, etc.
4.	High-level descriptions of various tasks, e.g. graphic operations, design procedures, specification-directed simulation, definition of design or operational goals, automatic modelling of process units, etc.
5.	Equation-oriented simulation and design facilities with dynamic generation of the relevant equations (specified by the problem to be solved), pre-processing of the equations, selection of the design variables, symbolic differentiation, etc.
6.	Reasoning capabilities for the utilization of heuristic knowledge, qualitative information, order-of-magnitude analysis, goal-directed design or planning, as well as query and explanation facilities
7.	Unified data base management system with contextual description of the information and capability, through a common data model, to handle all types of knowledge (data, graphs, equations, inequalities, procedures, qualitative statements, heuristics, etc.)

operability and economics; (3) the sizing and costing of major equipment; (4) the creation of control loop configurations; (5) the design for start-up, shut-down and alternative operating modes; and (6) the generation of piping and instrument diagrams, fabrication isometrics, etc. Further, the environment should allow high-level communication between the user and the computer, full and transparent integration of its various facilities, and easy maintenance and modification.

Some specific features of DESIGN-KIT are shown in Table 30.5.

30.32 Process Synthesis

Turning now to the actual design process, the most creative part of the design is the synthesis of the process and of the plant.

Accounts of process and plant synthesis have been given in *Strategy of Process Engineering* (Rudd and Watson, 1968) and in *Conceptual Design of Chemical Processes* (Douglas, 1988). Reviews include those of Westerberg (1980, 1985), Nishida, Stephanopoulos and Westerberg (1981), Umeda (1982), Stephanopoulos and Townsend (1986), Grossman and Floudas (1987), Gundersen and Naess (1988), Floquet, Piboleau and Domenech (1988), R. Smith and Linnhoff (1988), Grossman (1989) and Hutton, Waters and Ponton (1990).

The work of Rudd and Watson deals with in the first part, the creation and assessment of alternatives under the headings of (1) the synthesis of plausible alternatives, (2) the structure of systems, (3) economic design criteria, and (4) cost estimation; in the second part, optimization under the headings (5) the search for optimum conditions, (6) linear programming, (7) the suboptimization of systems with acyclic structure, (8) macrosystem optimization strategies, and (9) multilevel attack on very large problems; and in the third part, engineering in the presence of uncertainty under the headings (10) accommodation to future developments, (11) accounting for uncertainty in data, (12) failure tolerance, (13) engineering around variations and (14) simulation.

A series of studies on process synthesis have been described by Rudd and co-workers (Masso and Rudd, 1968, 1969; Rudd, 1968; Siirola, Powers and Rudd, 1971a, b; Powers and Jones, 1973; Rudd, Powers and Siirola, 1973; and May and Rudd, 1976).

Douglas (1988) describes a hierarchical approach to conceptual design with the following hierarchy of decisions:

(1) batch vs continuous;
(2) input–output structure of the flowsheet;
(3) recycle structure of the flowsheet;
(4) general structure of the separation system –
  (a) vapour recovery system,
  (b) liquid recovery system;
(5) heat exchanger network.

Douglas' work deals with: in the first part, a strategy for process synthesis and analysis under the headings (1) the nature of process synthesis and analysis, (2) engineering economics, and (3) economic decision-making; in the second part, developing a conceptual design and finding the best flowsheet under the headings (4) input information and batch vs continuous, (5) input–output structure of the flowsheet, (6) recycle structure of the flowsheet, (7) separation system, (8) heat-exchanger networks, and (9) cost diagrams and the quick screening of process alternatives; and in the third part, other design tools and applications under the headings (10) preliminary process optimization, (11) process retrofits, (12) computer aided design programs, and (13) summary of, and extensions to, the conceptual design procedure.

Process synthesis is of great importance. In particular, it is relevant to (1) inherently safer design, (2) inherently cleaner design and (3) inherently low energy design, or process integration.

30.32.1 Process route

If the process involves a chemical reaction, this reaction is generally the most fundamental feature of the process. A number of studies have been carried out with a view to developing computer aids to selecting the chemical route, or process synthesis. Such work has been described, for example, by May and Rudd (1976). This is an area with great potential which has barely been broached.

30.32.2 Process flowsheet

The synthesis of the overall flowsheet is the least developed area of process synthesis. Most work addresses the more tractable subproblems such as energy economy.

A prototype system for the synthesis of the process flowsheet, PIP, has been described by Kirkwood, Locke and Douglas (1988). PIP has a hierarchical structure. It utilizes heuristics to select unit operations, to establish interconnections between them, to identify the dominant design variables and to generate process alternatives. It attempts to devise a flowsheet using a depth-first search.

Beltamini and Motard (1988) have described the development of an expert system, KNOD, which acts as a front end to a process simulator. It is used to test strategies and heuristics for the design and simulation of process structures.

A method of synthesizing a flowsheet which combines hierarchical and algorithmic approaches is described by Mizsey and Fonyo (1990). A prime purpose of this system is to give the designer confidence that the initial universe of potential process paths generated contains all the relevant paths.

30.32.3 Process simulators and databases

It is now common practice to use a process simulator to explore the various features of a process flowsheet. This simulation brings with it a requirement for more powerful database systems which are capable of supporting such work. Conventional database management systems tend to be deficient in a number of ways and the development of database systems for process simulation has been an active area of work. An example is the development of SIMBAD, a process simulator linked to a powerful database, described by Montagna *et al.* (1987).

There is also a trend to add object oriented features to traditional relational databases. Huang and Fan (1988) describe a hybrid database which marries an object oriented approach with a relational one.

30.32.4 Process integration as a model

One of the most successful areas of process synthesis is that of process integration, the design of heat exchanger networks. Taking this as a model for process synthesis as a whole, Westerberg (1989) identifies two key features. One is the ability to set targets for the design and the other is the use of an effective domain-specific representation, in this case for heat flow.

30.32.5 Other process design aspects

The problem of handling constraints during design is addressed by Waters and Ponton (1992). The work is concerned with the early identification and correction of design errors and explores the use of an automated checklist to prevent violations of design intent.

An exploration of the applicability of an expert system to the design of batch processing systems is described by Hofmeister, Halasz and Rippin (1989). The authors refer particularly to the importance of problem representation, highlighted in the earlier work of Rippin (1983).

Hanratty and Joseph (1992) have described the application in an expert system for reactor selection of the analytic hierarchy process (AHP) method of Saaty (1980). The AHP is one of the techniques for encoding expert judgement, as described in Chapter 9, and is widely used in the social sciences. It is based on the method of paired comparisons.

Another design problem is the analysis of the flexibility of a design. This has been addressed by Grossman and Floudas (1987) who describe a flexibility criterion and a flexibility test.

Engelmann *et al.* (1989) have described the use of distributed expert systems in process synthesis.

30.33 Plant Design: Synthesis

Moving on to the design of the plant as opposed to that of the process, this too is an important area. Here some modest progress has been made in the development of aids for certain types of task, but there remains much scope.

30.33.1 Inherently safer design

One of the prime aims in the design of process plants is to promote the practice of inherently safer design right from the conceptual design stage. Apart from developments such as those in process synthesis and the selection of a reaction route, which are certainly important aspects of inherently safer design, it is not easy to identify any specific synthesis aid in this area.

30.33.2 Characteristics of design problems

An overview of the expert design of plant handling hazardous materials has been given by Bunn and Lees (1988). What these authors do is to describe a series of design problems, involving various kinds of design expertise, ranging from very simple, even trivial, design activities to designs with deep structure and to designs apparently better suited to solution by machine rather than by man.

The problems considered in this work are (1) the choice of whether or not to fit an emergency isolation valve, (2) the design of a flare system, (3) the design of a pressure relief system and (4) the design of a valve sequencing system; together in each case with the nature of the appropriate AI aid.

The first part of this section gives an account of this work, as an illustration of the potential for AI and expert system aids across the whole synthesis activity in plant design. The second part describes some particular aids which have been developed.

30.33.3 Design as equipment selection: emergency isolation valves

The most simple problem in the set considered by Bunn and Lees is the decision whether or not to fit an emergency isolation valve (EIV). The problem was investigated by studying a published paper in which an expert describes the factors which he took into account in making the decision and gives examples of cases where such valves were installed and of others where they were not. An interview was also held with the same expert.

The account used was that given by Kletz (1975b) of the installation of EIVs on two petrochemical plants. In deciding whether or not to install an EIV both the frequency and consequences of an escape were taken into account. Kletz' paper states:

> Three situations should be considered:
> 1. The equipment is particularly likely to leak; for example, very hot or very cold pumps.

Table 30.6 *Emergency isolation valve location: parameters for the provision of emergency isolation valves on an olefins plant (Bunn and Lees, 1988; after Kletz, 1975b) (Courtesy of the Institution of Chemical Engineers)*

Item	*Material*	*Temperature* (°C)	*Pressure* (psig)	*Inventory* (ton)	*Leak history*	*EIV*	*Note*
1. Furnaces	Naphtha	100	120	Small	–	Y	1
2. Feed pump	Naphtha (gassy)	15	140	70	N	N	2
3. Bottoms pump	Fuel oil	210	30	100	Y	Y	3
4. Sidestream pump	Distillate fuel oil	160	25	20	N	Y[a]	
5. Bottoms pump	Fuel oil	210	30	60	Y	Y	
6. Bottoms pump	Gasoline	85	20	25	–	N	4
7. Bottoms pump 1	Fuel oil	220	30	1	Y	N	5
2	Distillate fuel oil	180	25	1	–	N	5
8. Reflux pump	Ethylene	−30	270	30	Y	Y	6
9. Sidestream pump	Ethylene	−30	270	10	Y	Y	7
10. Reflux pump	Propylene	40	250	50	N	Y	
11. Cold Al exchanger	Methane	−100	370	30	Y	Y	8
12. Process gas compressor	Methane, ethylene, propylene, etc.	40	30	50	–	N	9
13. Compressor	Ethylene	−100	65	40	–	Y	9
14. Compressor	Propylene	−40	40	100	–	N	9
15. Bottoms pump	Light gasoline	90	150	5	Y	N	10
16. Reflux pump	Methane	−100	370	5	Y		11
17. Reflux pump	Ethane/ ethylene	−14	350	5	–		12
18. Converter	Ethane/ ethylene	80/150	350	–	Y	Y	13
19. Reflux pump	Propylene	5	90	1	–	N	
20. Reflux pump	Propylene	30	175	5	–	N	
21. Bottoms pump	Butylene	120	50	15	–	N	
22. Reflux pump	Butylene	35	50	5	–	N	

[a] Borderline.

Notes:

1. Control values used as EIVs in event of tube failure and reasonably remote hand isolations.
2. No history of leaks, material cold.
3. Close to autoignition temperature. Similar pumps have ignited.
4. Inventory can be pumped out with other pumps.
5. Inventory small and feed to column can be isolated.
6. Pump has leaked.
7. Pump has leaked and ignited.
8. AI heat exchangers more fragile than steel and therefore classified as likely to leak. Isolation by means of remote hand valves, control valves and one extra EIV.
9. Centrifugal machines – no history of leaks except one bad leak on ethylene compressor. Most of inventory would be flared. Leaks would be gas. Leak rate from ethylene and propylene compressors would be small – several tons per hour.
10. Congested area, but remote manual valve accessible.
11. Valve fitted remote by distance – but upstairs. Despite low temperature there is no history of leaks.
12. Valve fitted remote by distance – but upstairs.
13. Valve fitted on inlet and exit and blowdown lines to isolate and blow down vessel to stop runaway reactions. At least 5 incidents have occurred on plants outside the company.

2. The equipment is less likely to leak. But if it does leak, a very large quantity of material will run out and there is no way of stopping it; for example, the bottom pump on a still containing more than, say, 50 ton of flammable liquid.
3. The equipment is less likely to leak, but if it does so, the leak will be very large; for example, a very large pump.

Table 30.7 *Emergency isolation valve location: apparent influence of expert's rules on the decision to fit emergency isolation valves on an olefins plant (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

Item	*History of leaks*	*Fit EIV*	*Comment*
1. Furnaces	–	Y	Rule 1(c) apparently. Rule 5
2. Feed pump	N	N	Influence of counterrule 1(a), 3
3. Bottoms pump	Y	Y	Rule 1(a) and (b), 2, 3
4. Sidestream pump	N	Y[a]	Rule 1(a) and (b) and 2 not satisfied, but influence of Rules 2 and 4 perhaps
5. Bottoms pump	Y	Y	Rule 1(a) and (b), 2
6. Bottoms pump	–	N	Rule 6
7. Bottoms pump 1	Y	N	Rule 1(a) and (b) but overridden by Rule 6
2	–	N	(Rule 1(a) and (b) not satisfied)
8. Reflux pump	Y	Y	Rule 1(a) and (b)
9. Sidestream pump	Y	Y	Rule 1(a) and (b)
10. Reflux pump	N	Y	Rule 2 apparently
11. Cold Al exchanger	Y	Y	Rule 1(a) and (b). In part Rule 5
12. Process gas compressor	–	N	Rule 7
13. Compressor	–	Y	Rule 7 but overridden by Rule 4
14. Compressor	–	N	Rule 7
15. Bottoms pump	Y	N	Rule 1(a) but overridden by Rule 6. Influence of counterrules 2 and 3 perhaps
16. Reflux pump	Y	?	Meaning of notes not clear. Does
17. Reflux pump	–	?	valve fitted refer to existing valve?
18. Converter	Y	Y	Special case
19. Reflux pump	–	N	(Rule 1(a) and (b) and 2 not satisfied)
20. Reflux pump	–	N	As (19)
21. Bottoms pump	–	N[a]	As (19)
22. Reflux pump	–	N	As (19)

[a] Borderline.
Note: Extremes of temperature taken as $-30^{\circ}C < T > 180^{\circ}C$.

The paper gives two tables, one for an olefins plant and one for an aromatics plant, listing the situations where the installation of an EIV was considered, giving the parameters for these situations and stating whether or not it was decided to install such a valve. One of these tables, that for the olefins plant, is shown in Table 30.6.

From the rules explicitly stated, the examples given and the comments made in the text of the paper, the following extended set of rules was derived. The overt rules are:

(1) Fit if the equipment is particularly likely to leak. This is so if (a) it has a history of leakage or (b) it is pumping liquid at extremes of temperature or (c) it is otherwise thought likely to leak.
(2) Fit if the equipment is less likely to leak, but if it does, it could release a large or very large quantity.

There also appeared to be some covert rules. These include:

(3) Fit if the liquid is above its autoignition temperature.
(4) Fit if it is convenient for process reasons.
(5) Do not fit if there is a control valve which will perform the same function.
(6) Do not fit if there is an alternative means of stopping the leak.
(7) Do not fit if the fluid is a gas in a compressor.

Here the second and third rules given by Kletz have been combined into a single rule.

Some of the rules are stronger than others. Thus Rule 1 is a strong rule. Rules 5 and 6 are also strong rules. Rule 7 is a weak rule and may be overriden by Rule 4. A particular rule also seems to have some influence as a counter-rule. Thus a small inventory weights the decision against fitting an EIV. An analysis of the apparent effects of the rules is shown in Table 30.7

The decision on whether to provide an EIV appeared to be a relatively straightforward classification problem. The use of an AI aid for classification was therefore investigated, the programs chosen being initially EXPERTEASE and later EXTRAN, which are based on the ID3 algorithm.

The class value was taken as EIV fitted/not fitted; and the attributes as (1) fluid, (2) equipment, (3) inventory, (4) temperature, (5) pressure and (6) leak history. The first and second attributes were entered as the process material and the plant equipment, the third to fifth attributes as a number and the last attribute as yes/no.

Table 30.8 *Emergency isolation valve location: revised formulation of parameters for the provision of emergency isolation on an olefins plant (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

	Attribute[b]								
Item	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*EIV*
1. Furnaces	N	Y	N	N	N	N	N	–[a]	Y
2. Feed pump	N	N	Y	N	N	N	N	–[a]	N
3. Bottoms pump	Y	N	N	Y	Y	N	N	–[a]	Y
4. Sidestream pump	N	N	Y	N	Y	N	N	–[a]	Y[a]
5. Bottoms pump	Y	N	N	Y	Y	N	N	–[a]	Y
6. Bottoms pump	N	N	N	N	N	Y	N	–[a]	N
7. Bottoms pump 1	Y	N	N	Y	N	Y	N	–[a]	N
2	N	N	N	Y	N	N	N	–[a]	N
8. Reflux pump	Y	N	N	Y	N	N	N	–[a]	Y
9. Sidestream pump	Y	N	N	Y	N	N	N	–[a]	Y
10. Reflux pump	N	N	N	N	Y	N	N	–[a]	Y
11. Cold Al exchanger	Y	N	N	Y	N	N	N	–[a]	Y
12. Process gas compressor	N	N	N	N	N	N	Y	–[a]	N
13. Compressor	N	N	N	N	N	N	Y	Y	Y
14. Compressor	N	N	N	N	N	N	Y	–[a]	N
15. Bottoms pump	Y	N	N	N	N	Y	N	–[a]	N
16. Reflux pump	Y	N	N	N	N	N	N	N	(1)
17. Reflux pump	Y	N	N	N	N	N	N	N	(1)
18. Converter	Y	N	N	N	N	N	N	–[a]	Y
19. Reflux pump	N	N	N	N	N	N	N	–[a]	N
20. Reflux pump	N	N	N	N	N	N	N	–[a]	N
21. Bottoms pump	N	N	N	N	N	N	N	–[a]	N
22. Reflux pump	N	N	N	N	N	N	N	–[a]	N

[a] Borderline.
[b] Attributes:
1. Does the equipment have a history of leaks?
2. Is the equipment otherwise likely to leak?
3. Is the liquid above its autoignition temperature?
4. Is the liquid being pumped at high temperature?
5. Is the equipment less likely to leak, but the situation such that if it does a large quantity will escape (is there a large hazard)?
6. Is there an alternative means of stopping the leak?
7. Is the fluid a gas in a compressor?
8. Is the fitting of an EIV convenient for process reasons?

Table 30.9 *Emergency isolation valve location: set of rules for the provision of emergency isolation valves on a alkenes plant (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

large hazard
  yes: fit EIV
  No: leak history
    Yes: fit EIV
    No: otherwise likely to leak
      Yes: fit EIV
      No: pumping at high temperatures
        Yes: alternative means of stopping leak
        No: fit EIV
Otherwise no EIV

The 22 cases were run through the program which induced from them a set of rules. However, this first application was not regarded as satisfactory. Among other things, no use was made of leak history, which was supposed to be a strong rule.

The view was taken that the problem should be reformulated. This time the attributes taken were (1) large hazard, (2) leak history, (3) high leak likelihood, (4) large inventory, (5) high temperature, (6) above the autoignition temperature, (7) convenient for process reasons, (8) alternative means of stopping the leak and (9) fluid is a gas in a compressor. The revised data set is shown in Table 30.8 and the set of rules induced is given in Table 30.9.

This set of rules was regarded as more satisfactory. However, in view of the fact that Rule 6 is a strong rule, it was considered that it should probably be the first branch. The fact that this is not so is evidently due to the fact the example set is not sufficiently comprehensive.

The authors conclude from this example that an AI classification tool of this general type can be useful, but that it has to be applied with caution. Care needs to be taken in the definition of the attributes and in the

Table 30.10 *Design of flare systems: some aspects of the design expertise involved (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

General area	*Specific element or topic*
Gas flows requiring disposal	Normal flows Emergency flows
Gas compositions requiring disposal	Hydrocarbons Hydrogen Hydrogen sulphide Steam Air
Alternatives to flaring	Total containment Trip systems Relief valve venting to atmosphere (air, steam, cold gases) Unflared vent stacks Plant specific flaring
System options	Multiple flare systems Dry gas vs wet gas High vs low level flares Controlled blowdown
Segregation	Dry gas vs wet gas High or low temperature gases Hydrogen sulphide Reactive materials
Flare system, basic elements	Relief header Knockout drum Seal drum Flare stack Flare tip Pilot light
Flare system, additional elements	Quench drum Vaporizer drum Vapour recovery Flame arresters Molecular seals
Purge gas	Fuel gas Nitrogen
Hazards	Blockage Explosion Heat radiation Toxic gases Liquid carryover
Air hazard	Sources Effects
Water hazard	Sources Effects
Extreme cold	High melting point hydrocarbons Steam injection
Other problems	Ignition failure Smoke Pollution Glare Noise Land sterilization
Legislation	Pollution control Smoke Noise
Standards, codes	Plant layout codes BS CP 3013: 1974 API RP 520 API RP 521 1969
Knockout drum design	
Flare stack design	Diameter Height
Flare tip design	Steam Low pressure air Coanda flares
Design models	Flame dimensions Heat radiation Buoyant plume (ground level concentrations)
Evaluation criteria	Heat radiation levels Smoke levels Noise levels
Economics	Relief header costs Flare stack costs Other equipment costs Purge gas costs Land sterilization
Optimization	Capital vs operating costs Land sterilization Controlled blowdown Purge gas costs
Project control	Long lead items
Materials of construction	Corrosion Brittle fracture
Mechanical construction	Welded joints Header valves Insulation, steam tracing
Explosion prevention	Inert gas flow Inert gas conservation, molecular seals Oxygen monitoring Flashback prevention, flame arresters
Process control	Controlled blowdown Manual vs automatic control of flare quality
Start-up	Initial purge with inert gas High gas flows
Shut-down	Air diffusion
Turn-down	Low gas flows High gas flows
Emergency conditions	

Continued over

Plant operation	Operating instructions Emergency action (to reduce flows)
Plant maintenance	
Plant extensions	
Plant modifications	

provision of a learning set which is not only sufficiently large but also is specifically designed to cover the domain.

30.33.4 Designs with shallow structure: flare system

The next problem considered by Bunn and Lees is the design of a flare system. They take this as representative of a class of design synthesis problems with relatively shallow structure.

A common design problem is the design of a unit for which there already exists a skeletal design archetype, or stereotype, which is more or less fixed in respect of the basic set of components, but where there exist options both for the details of these components and for add-on features. If it is assumed that all the relief gas flows which are to be handled have already been specified then, the authors argue, flare design might be taken as an example of this type of problem.

Generally, the first step taken by the expert is to define the primitive problem. The understanding that the problem originally posed needs to be redefined and the ability to do this is an essential feature of his expertise. In order to do this he needs to collect information. In the case of a flare system this includes data on gas flows and composition. He is then able to consider whether alternatives to flaring are appropriate. These include, in the case of a flare system, total containment, trip systems, relief valve venting to atmosphere, unflared vent stacks and plant flaring.

Given that a flare system is still the appropriate solution for at least some of the relief flows, the expert has then to determine a strategy for the overall system. This may involve controlled blowdown to smooth out peak flows, low and high level flares and multiple flares. A particular aspect of this strategy is segregation of different gas flows: dry from wet gases, normal temperature from low temperature gases, hydrogen sulphide from other gases, and reactive gases from other gases. Only when these various strategic decisions have been made does the design of the flare system itself begin. Some aspects of the design expertise involved in flare system design are outlined in Table 30.10.

A typical flare system is illustrated in Figure 30.11. The basic elements of a flare system are the relief header, the knockout drum, the seal drum, the flare stack, the flare tip and the pilot light. The design of the flare system itself involves: deciding whether to provide various additional features; selecting a means of implementing the basic and additional features both in terms of equipment and of utility fluids such as purge gas and flare tip steam; and a determination of the magnitude of some of these features. Possible additional features include quench drums, vaporizer drums, vapour recovery, molecular seals and flame arresters. Some principal features which need to be specified quantitatively include knockout drum size, flare stack diameter and height, flare tip dimensions, purge gas flow and flare tip steam flow. As Table 30.10 indicates, there are many further aspects which must also be taken into account.

Nevertheless, in the case of a flare system the basic structure of the design appears relatively straightforward. The design can apparently be decomposed into a set of

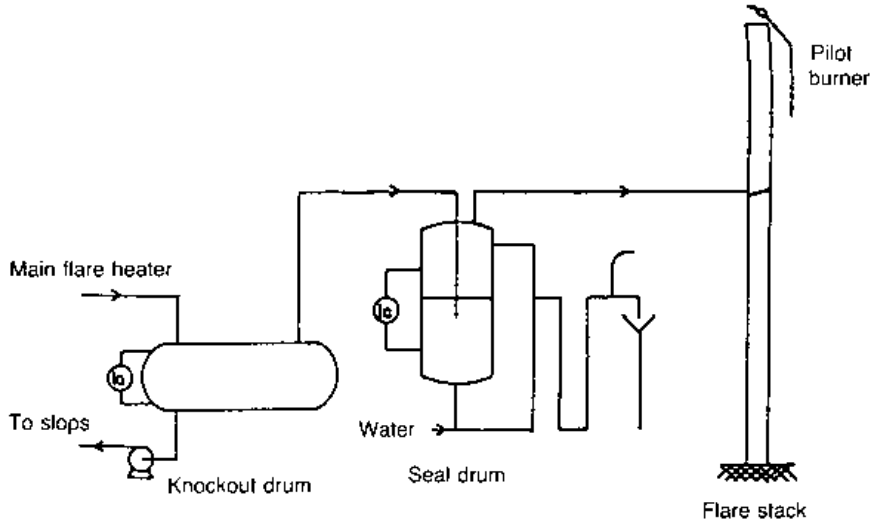


Figure 30.11 *A typical basic flare system (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

Table 30.11 *Design of pressure relief systems: outline strategy of system design (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

Decompose pressure system
Select subsystems
(Default assumption: each main vessel is a subsystem)
Identify pressure breaks
Locate pressure reliefs
(Default assumption: pressure relief is located on each main vessel)
Identify relief loads on each main vessel
Utility failure (including control loop failures)
Open inlet (connection to high pressure source)
Closed outlet (disconnection to low pressure sink)
Heat input
Cooling loss
Operating excursions
Equipment failures (especially valves: NRVs, EIVs)
Fire
Quantify relief loads on each main vessel
Utility failure standard cases
Fire standard cases
Select relief sink
Other part of plant
Flare header
Other closed system
Atmosphere
Determine set pressure of RVs
Determine capacity of RVs
Select type of RVs

EIV, emergency isolation valve; NRV, non-return valve; RV, return valve.

subdesigns which have only weak interaction. The design may proceed in a series of sequential stages, using rules appropriate to each stage, and with only a modest degree of iteration.

Bunn and Lees list a number of rules obtained from the literature, from standards and codes and from expert sources, which are used in flare system design. They classify these rules as follows:

Alternative (A) An alternative option is offered.

Requirement (R) A requirement to take a particular course of action, add a particular feature or achieve a particular result.

Permission (Pe) A permission to take a particular course of action or add or omit a particular feature.

Prohibition (Pr) A prohibition on taking a particular course of action or adding a particular feature.

Design (D) A rule of thumb giving guidance on some particular aspect, usually a design criterion.

A prohibition is essentially a negative requirement.

The derivation and use of the rules revealed several problems, which were not unexpected. One is that the abstraction of rules from the literature is liable to give rules which are contradictory or out of date. Another is that some rules are stronger than others and a means needs to be found to incorporate this factor. Similarly, some rules are subject to exceptions and this also needs to be taken into account.

The authors identify the following types of expertise as being involved in flare system design:

(1) knowledge of the initial data to be collected;
(2) knowledge of the ways in which the primitive problem may be reformulated;
(3) knowledge of the alternatives to the use of a flare system and of criteria for their selection;
(4) knowledge of options for modification of the flare load to be accepted;
(5) knowledge of the basic configurations of flare systems;
(6) knowledge of the options for additional features and criteria for their selection;
(7) knowledge of the models available for the design of particular features and of the regimes in which they apply;
(8) knowledge of the constraints associated with regulatory controls, standards and codes, and so on.

The authors refer to the creation of a simple research expert system for elementary flare system design incorporating a rule-based production system. The program described uses forward-chaining and the principal conflict resolution methods are context limitation and specificity ordering.

Although the flare design problem is classed by the authors as one with shallow structure, this emphatically does not mean that it is straightforward. The classification refers solely to the structure of the problem and the decomposition required to solve it. In fact, the design rules used by an expert may well be very sophisticated. The point is that the expertise resides in these other rules rather than in rules, or strategies, for decomposition.

30.33.5 Designs with deeper structure: pressure relief system

Bunn and Lees' third problem is the design of a pressure relief system. This problem they take as representative of a class of design synthesis problems with relatively deep structure.

The situations which are considered for pressure relief are operational relief, both normal and abnormal, and fire relief. A relief survey is made based on the piping and instrument diagram. The system is decomposed into subsystems. The decomposition is done on the basis of what is manageable. Typically a subsystem is a functional unit, such as a distillation unit, with up to half a dozen vessels. Another principle which is used is that of pressure breaks, the section of plant between two such breaks being for practical purposes at a uniform pressure level.

A review is made for operational relief of the overpressure sources and load to be relieved. This covers: utility failures, where use is made of standard cases; open inlets and closed outlets; heat inputs; cooling loss; operating excursions; and equipment failures. For fire, a finer subdivision may be used, with a separate consideration of each vessel. Again use is made of standard cases.

Selection is made of the relief sinks, which may be another part of the plant, the atmosphere, the relief header, or another closed system. The capacities and set pressures of the pressure relief valves may then be determined and the pressure relief valves selected.

Table 30.12 *Design of pressure relief systems: some aspects of overpressure sources and loads (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

Overpressure sources	*API RP 521 (page no.)*
1. Extraneous components:	
Water in hot oil	9
Light hydrocarbon in hot oil	9
Light components in distillation fluids	7
2. Chemical reactions:	
Combustion	11
Reaction runaway	12
3. High pressure (HP) source:	
HP process fluids	4
HP utilities	4
Pressure raisers	
Pumps	
Compressors	
Heat exchanger HP side	5.15
4. System isolation:	
Systems with closed outlet	4, 7
Shut-in systems (see thermal expansion below)	
5. Heat input:	
Burners	
Steam	5
Heat transfer fluid	
Atmosphere	
6. Cooling loss:	
Water cooling	
Cooling water failure	8
Flooding	8
Inerts accumulation	8
Air cooling	
Fan failure	8
Louvres failure	8
Heat transfer fluid	
Reflux cooling	
Reflux pump failure	8
Subcooled feed	
7. Thermal expansion (shut-in systems):	
Fluid at ambient temperature	12
Fluid below ambient temperature	12
Fluid below temperature of another process fluid	12
8. Pressure transients:	
Water hammer (incompressible fluid)	6
Steam hammer	6
9. Fire	6, 13
Relief loads	
Single failure principle	
Control loop effects	
Capacity credit	
Utility failure standard cases	
Fire standard cases	

Table 30.13 *Design of pressure relief systems: some additional topics to be considered (Bunn and Lees, 1988) (Courtesy of the Institution of Chemical Engineers)*

A list of areas of expertise, by no means complete, is:

Legal and standards requirements
Alternatives to or mitigation of PR:
  Pressure containment
  Pressure limiting instrumentation
Mitigation of fire PR:
  Fireproofing
  Water drench
  Ground slope
Pressure limiting instrumentation:
  Alternative to PR
  Mitigation of PR
    Reduction of flow
    Reduction of frequency
  Standard applications
Economics of alternative solutions
Overpressure scenarios:
  Utility failure standard cases
  Fire standard cases
Unit operations and equipment:
  Furnaces
  Distillation columns
  Shell and tube heat exchangers
  Air cooled heat exchangers
  Centrifugal pumps
  Pressure storage
  Steam systems
  Pipelines
Selection of disposal systems:
  Other parts of plant
  Flare system
  Other closed system (e.g. absorber)
  Atmosphere
Atmosphere disposal:
  Disposal criteria
  Safe disposal
    PRV design and location
Flare disposal:
  Segregation of materials
  Materials of construction
Minimum venting pressure:
  Flare header
  Atmosphere
Depressurizing arrangements
Special conditions:
  Corrosive fluids
  Cold fluids
  Fluids containing hydrogen sulphide
Stepped relief settings
Selection of PRVs
Thermal relief
Hammerblow prevention
Vacuum relief

PR, pressure relief; PRV, pressure relief valve.

The foregoing is the barest outline of the design process for pressure relief. It is summarized in Table 30.11.

Some of the topics which may be considered in the review of overpressure sources and loads are listed in Table 30.12. Some of the additional topics which also need consideration are listed in Table 30.13.

The design of pressure relief systems appears therefore to involve appreciable expertise in the selection of a design strategy. There is, in principle, a significant initial decomposition to be performed. Knowledge is required of the range of overpressure sources which need to be reviewed. Some of these are effectively stereotype situations. A credible worst case has to be selected. In making this selection, both for utility failure and for fire, use is made of standard cases to prevent the design worst case being too pessimistic. There is a whole range of design alternatives to be considered and of special situations to be taken into account.

A common strategy for handling problems with deeper structure is to apply a small number of additional rules which simplify the decomposition. In the case of pressure relief system design one such rule is to provide each vessel with a pressure relief valve.

30.33.6 Designs with deeper structure: valve sequencing

The final problem in design synthesis considered by Bunn and Lees is that of valve sequencing. This problem is taken as being representative of a class of design synthesis problems which are characterized by the features that there is a complex problem-solving task, but that this task requires little expertise or common sense knowledge.

The generation of an operating sequence for a set of valves, subject to certain constraints, is very similar to the problem-solving and game-playing tasks commonly addressed in AI. It involves a search to satisfy goals. The knowledge which has to be provided to obtain a solution is, however, relatively limited.

These features imply another characteristic of this type of problem. There tends not to be a recognized expertise. There is provided as part of the design a network of valves which need to be opened and shut in order to operate the plant. An engineer is assigned the task of specifying the operating sequence, but this assignment is unlikely to be made on the basis of a recognized expertise comparable with, say, expertise in flare system design.

Bunn and Lees instance here the work of Rudd and co-workers on the synthesis and analysis of valve sequences. This study is described in Section 30.43 along with other work on the synthesis of operating sequences. This example completes the overview of some characteristic design synthesis problems. The remainder of this section describes some of the design aids which have been developed.

30.33.7 AI applications

Turning now from the structure of plant design synthesis problems to applications of AI to such synthesis, an account of AI applications which deals particularly with plant synthesis and analysis as well as process synthesis is given by Hutton, Ponton and Waters (1990).

At present most such applications appear to be in the area of expert systems. Some of these are considered in Section 30.35. However, the current consensus appears to be that the most promising methods are those which are based on process modelling of the sort described in Section 30.30.

30.33.8 Incremental design and safety constraints

A development of some interest is the concept of incremental design as applied to safety. In conventional plant design, the designers proceed with the design, adhering to good design practice, and the design is subjected to safety reviews at prescribed stages. An alternative approach, which emphasizes the application of the safety constraints in an incremental way, has been championed by Ponton and co-workers. The application of this philosophy has been described in respect of the safety constraints on design by Waters, Chung and Ponton (1989) and Waters and Ponton (1992) and in respect of hazard studies by Black and Ponton (1992).

30.33.9 DSPL

Another development is the application of methods developed for equipment design to the design of process plant. An account was given in Section 30.27 of the expert system building tool DSPL. This has been used mainly for mechanical design, but in the process field DSPL has been used by Myers, Davis and Herman (1988) to create an expert system for the design of sieve plate distillation columns.

30.34 Plant Design: Analysis

The synthesis of plant designs is complemented by their analysis. The analysis constitutes the test element in the overall generate-and-test activity. There now exist a large number of computer programs for the analysis of various aspects of plant design. One category is those programs which compute an index and perform a ranking of the hazards of the plant. Another category is those which assist with hazard assessment. Computer aids of this sort have been described in Chapter 29. There are now beginning to appear aids for design analysis which have an AI flavour.

30.34.1 Inherently safer design

Although aids for the synthesis of inherently safer design are not well developed, some work has been done in analysing of plant designs to check the extent to which they conform to this principle. A program of this nature has been developed by Journet (1993). The process is treated as an object or frame and the features of the process and the plant are developed as a hierarchy. Early branches in the hierarchy are the chemical route, the design information, the process streams, the plant units, the nomenclature and the decisions. The treatment is informed by the concepts of elimination, substitution, intensification and attenuation. The program identifies the features with implications for an inherently safer design.

30.34.2 Fault propagation

A number of aids to plant analysis have been described which are based on the qualitative modelling of the propagation of faults through the plant. Fault propagation modelling is therefore a basic enabling technology. It is described in Section 30.36.

30.34.3 Hazard identification

One aspect of plant analysis which has attracted much interest is the creation of an aid to hazard identification which would produce information similar to that yielded by a hazop study. Developments in this area are described in Sections 30.37–30.39.

30.34.4 Fault tree analysis

Another aspect of plant analysis which has attracted a number of workers is the development of an aid for the synthesis of fault trees. Programs have been available for some years for the analysis of fault trees, but the construction of the fault tree is still done manually. Developments in this area are described in Sections 30.41 and 30.42.

30.35 Expert Systems: Some Process Systems

Expert systems were introduced in the process industries in the mid-1980s and are in widespread use. The typical expert system in the process industries is much more modest than the classic expert systems described in the previous section. Most have been created using shells. An appreciable proportion have been developed by a single engineer acting as the expert. The development time has generally been of the order of months rather than years.

Some principal applications are: (1) physical, chemical and thermodynamic properties; (2) selection of equipment, materials of construction, and processes and plants; (3) design of processes and plants; (4) process control; (5) process monitoring; and (6) fault administration. The first four of these are considered in this section and the last two in Sections 30.44 and 30.45.

The bulk of these applications is to the handling of fault conditions, either on an individual item of equipment or on a process plant. Before considering these different application areas, it is of interest to consider a statistical profile of process industry applications.

30.35.1 Statistical profile

A survey of expert system applications in the process industries has been described by Sangiovanni and Romans (1987).

These authors found about 200 applications in some 30 companies. They classified these applications as (1) selection, (2) design, (3) planning and scheduling, (4) control, (5) situation analysis, (6) diagnosis, (7) prediction, (8) prescription and (9) instruction. They define: situation analysis as monitoring available data and information and inferring the system's state; diagnosis as inferring the cause of a malfunction or deviation; prediction as inferring the likely consequences of an action or set of actions; and prescription as recommending cures for a system malfunction or deviation.

Of these functions, selection accounted for some 15%. Situation analysis accounted for some 8%, diagnosis for 33%, prediction for 10% and prescription for 21%. Thus one-third of the applications were for diagnosis and the group of four functions related to fault administration (situation analysis, diagnosis, prediction and prescription) accounted between them for 66%. Only about 2% of applications were to design.

Of these expert systems, 30% had been developed by engineers, 29% by a team without the vendor, 29% by a team with the vendor and 12% by an internal AI group. The development time was <3 months for 30% 3–12 months for 40% and >12 months for 27%.

Some two-thirds of the systems were in daily use, including cases where the system was used by different people at a number of locations.

Some 90% of applications made use of an expert system shell. Over 60% were implemented on a PC. The dominant contributor to software costs was maintenance of the software, at some 67%, compared with design and coding and with testing and debugging, which each accounted for about 13%.

30.35.2 Physical, chemical and thermodynamic properties

An expert system for physical properties has been described by Banares-Alcantara, Westerberg and Rychener (1985). This system, CONPHYDE, uses the framework of PROSPECTOR and is described as a prototype. It has been applied to the selection of vapour–liquid equilibrium properties.

Gani (1989) has described an expert system for the selection of models of physical properties and phase equilibria.

30.35.3 Selection of equipment

An application of expert systems which has found rapid acceptance in the process industries is equipment selection. Many such applications utilize an induction tool which is provided by an expert with a learning set of examples, and induces the rules which the expert has evidently used in the solutions. This type of tool allows the expert to create his own system, and many experts have taken advantage of this. Equipment selection applications are not, however, confined to the use of induction tools. In other cases use has been made of shells.

An expert system for control valve selection has been described by Royse (1988). ICI has developed an expert system SYSLAG for the selection of thermal insulation (R.A. King, 1986).

30.35.4 Selection of materials of construction

The selection of materials of construction has been an active area of application. Accounts have been given by Baker-Counsell (1985b), Basden and Hines (1986) and R.A. King (1986).

An expert system for general corrosion has been developed by the National Association of Corrosion Engineers (NACE) and the National Bureau of Standards (NBS). Another such system, Achilles, has been created at Harwell. These systems are outlined by R.A. King (1986).

The Achilles system advises on the selection of mild steel and stainless steel for pipes, vessels and bolt assemblies. It exploits the use of graphics to illustrate the system under consideration and to highlight potential corrosion problems.

Expert systems used at ICI are outlined by Berkovitch and Baker-Counsell (1985). One of these is SCC for stress corrosion cracking. Another is AUSCOR for the selection and corrosion properties of stainless steels.

30.35.5 Selection of process and plant

There are also a number of expert systems for the selection of a process or plant, or an ancillary feature.

Lahdenpera, Korhonen and Nystrom (1989) have described an expert system for the selection of solid–liquid separation equipment. An expert system, DECADE, for catalyst selection has been created by Banares-Alcantara, Westerberg *et al.* (1987) and Banares-Alcantara, Ko *et al.* (1988)

30.35.6 Design of process and plant

Process synthesis and plant design, including high level expert system approaches, are considered in Sections 30.32–30.34. In general, design is a difficult application and there are relatively few examples of expert systems in design, as opposed to selection.

An expert system for the design of heat exchanger networks has been described by B. Chen *et al.* (1989). This is an area of design where a well structured approach has been developed so that the difficulties of creating an expert system are less severe.

Accounts of an expert system for the design of dust explosion relief systems have been given by Santon *et al.* (1991) and Santon (1992). Another expert system, DUSTEXPERT, for the assessment of dust explosion hazards has been described by von Haefen (1992).

30.35.7 Process control

Most applications of expert systems on process plants involve some form of process monitoring and/or fault administration rather than process control as such.

Work on the development of expert systems for the synthesis of control systems has been described by Birky, McAvoy and Modarres (1988) and Birky and McAvoy (1990).

The LINKMan expert system developed by the Scientific Instrument Research Association (SIRA) and the Blue Circle cement company has been used for control of equipment on the latter's plants. Accounts have been given by M. Henry (1985), Durham (1985f) and Tayler (1987b). Applications have included the control of a ball mill and of a cement kiln. The program uses rules for process control based on natural language and fuzzy logic.

The RESCU project (Shorter, 1985; Coulsey, 1986) involves the use of an expert system for the quality control of an ethoxylate plant in ICI. The system detects control variations and upsets, and recommends actions. One outcome of this project has been the development of the knowledge representation language KRL.

A follow-up to this work is the COGSYS system (Anon, 1988n).

PICON is an expert system with capabilities both in process control and also in fault administration. Accounts have been given by R.L. Moore (1985) and F. Kane (1986). Since the first applications have evidently involved fault administration, discussion of PICON is deferred to Section 30.45.

30.35.8 Other applications

Expert systems are in use in the process industries for a variety of other purposes. Reviews of applications and potential applications are given by M. Henry (1985), Coulsey (1986) and Barnwell and Ertl (1987).

The SYNICS system (Coulsey, 1986), which is described as not so much an expert system as a 'working textbook', containing both graphics and mathematics, is used both for problem-solving and browsing. Applications have included powder formulations.

The Honeywell MENTOR expert system (Sangiovanni and Romans, 1987) is used in the field by technicians servicing refrigeration systems.

30.36 Fault Propagation

Many of the methods used to identify and assess hazards at the design stage such as hazard and operability studies, failure modes and effects analysis, fault trees and event trees, involve tracing the paths by which faults propagate through the plant. Fault propagation is thus a common feature of these techniques. Fault propagation is also a feature of methods for the diagnosis of alarms in the real-time computer control of processes.

Fault propagation is therefore a generic feature of work in this field. It follows that the computer aids for many of these methods may, in principle, draw on a methodology which is to some extent common. This concept has been elaborated by Andow, Lees and Murphy (1980).

In the following sections computer aids are described for hazard identification, fault tree synthesis and analysis, and alarm diagnosis. Included in this account are some aids developed by Lees and co-workers which explicitly draw on a common methodology (Andow and Lees, 1975; B.E. Kelly and Lees, 1986a-d; Parmar and Lees, 1987a,b; A. Hunt *et al.* (1993a–e). Some features of the fault propagation methodology used in this work are now described.

30.36.1 Fault propagation

The propagation of a fault through a plant may be represented in terms of the initiation of a fault in a unit which is unhealthy, the passage of the faults through units which are otherwise healthy and the termination of the fault in a unit which is thereby rendered unhealthy. A unit may be modelled using a number of representations. Those considered here are: (1) functional, or propagation, equations; (2) event statements; and (3) decision tables.

The propagation equations describe the propagation of faults through a healthy unit, while the event statements describe the initiation of a fault in an unhealthy unit or the termination of a fault in a unit which thus becomes unhealthy.

A propagation equation is a functional equation which describes the relation between an output parameter of a unit and the input and other output parameters. A typical propagation equation is

$$L = f(Q_1, -Q_2) \qquad [30.36.1]$$

which signifies that the level L increases if the inlet flow Q_1 increases or the outlet flow Q_2 decreases, and vice versa.

30.36.2 Fault initiation and termination

The propagation equations describe how a fault propagates but not how it is initiated or terminated. This information is provided by event statements. An initial event statement takes the form

Initial fault: parameter deviation

The initial faults are usually mechanical failures. A terminal event statement takes the form

Parameter deviation: terminal event

The terminal events are usually undesired events or hazards.

A typical initial event statement is

F PART-BLK: Q_2 LO [30.36.2]

which signifies that outlet flow Q_2 is low if there is a partial blockage. The letter F denotes a failure event.

A typical terminal event statement is

P_2 HI: OVERPRES [30.36.3]

which signifies that if the pressure P_2 is high, there is overpressure of the unit.

The third form is a decision table. A typical decision table is

V Q_2 REV V U_2 HI T U_1 HI [30.36.4]

This relation refers to conditions in reverse flow, U being the temperature in reverse flow and subscripts 1 and 2 denote the inlet and outlet ports under normal flow conditions, respectively. The relation signifies that the outlet temperature U_1 is high if there is reverse flow Q_2 and the inlet temperature U_2 is high. The letters T and V denote the top event of a mini-fault tree and a process variable, respectively.

30.36.3 Flow propagation

In fault propagation modelling it is necessary to have a suitable method of modelling flow propagation. There are several features which need to be allowed for. One is that the representation should model correctly the two-way propagation of a fault. Thus, for example, if a valve is shut, a disturbance travels from it not only downstream but also upstream. The method for flow deviations should be compatible with that used for pressure deviations. A flow model which is based on pressure differences can run into difficulty because in some applications the deviations of pressure are not sufficiently well defined to use differences between them to determine flow. A third requirement in some cases is that the flow propagation should be able to handle a large leak from a component such that continuity of flow through that component is not maintained.

In cases where this latter aspect does not need to be taken into account, flow is often modelled by the simple relation

$$Q_2 = f(Q_1) \quad [30.36.5]$$

For the case where a large internal leak needs to be allowed for, Kelly and Lees (1986a) have modelled flow propagation using, by convention, the following pair of relations:

$$Q_2 = f(G_1,\ G_2) \quad [30.36.6]$$

$$G_1 = f(Q_1,\ Q_2) \quad [30.36.7]$$

where G is the pressure gradient, and Q is the flow and subscripts 1 and 2 denote the inlet and outlet ports, respectively. Here the pressure gradient G is essentially a surrogate for flow.

30.36.4 Model representation

Fault propagation models may be represented in various ways, which may well be equivalent.

Lees and co-workers (B.E. Kelly and Lees, 1986c,d; Parmar and Lees, 1987a,b) have represented their models initially in terms of propagation equations, event statements and decision tables. They have utilized a proforma which contains slots for a description of the unit and for these relationships. An example of such a proforma is given in the next section.

Most workers, however, have used the digraph representation. An account of digraphs has been given in Section 30.23.

The two representations, are in principle, equivalent. In digraph terms, the propagation equations yield those nodes in the digraph which represent deviations of the process variables and the initial event statements those nodes which represent failures.

The essential requirements for a model format are that (1) the modelling process be straightforward, so that it can be applied by practising engineers as well as research workers, with as little effort and error as possible, and that (2) it support the automation of model creation using model archetypes.

30.36.5 Model library

Models already created are stored in a model library. An essential feature of such a library is a taxonomy which helps the user to distinguish between different models and to identify those required or, alternatively, to confirm that some are not available in the library. The library needs to be governed by a discipline which ensures that appropriate information is provided about each model, such as the person creating it and the extent of its use, and that an incorrect model is not entered.

30.36.6 Model generation

Generally the user will find that some models are not in the library and need to be generated. In this case it is necessary to configure the models and enter them into the library. Since this is liable to be the main and most difficult input which the user has to provide, it is highly desirable that the process of model generation be kept as simple as possible.

The rules governing the manual generation of models should be formulated explicitly and documented.

In many cases the new model to be created differs only slightly from an existing one. There is therefore scope for the use of model archetypes and templates and for core models or model sections. This applies particularly to vessels. It is often the case that the model library already contains the models required for common items such as pipes, fittings, pumps, etc., and for instrumentation, but that there are certain vessels which need to be modelled. There is therefore scope for the provision of vessel archetypes and templates. Of particular significance here are ports on vessels and other units. Although there are a considerable number of different types of port, a given type tends to recur. It is useful therefore provide a taxonomy of ports and a guide to their selection.

Core model elements may be provided for common types of unit such as heat exchangers and reactors.

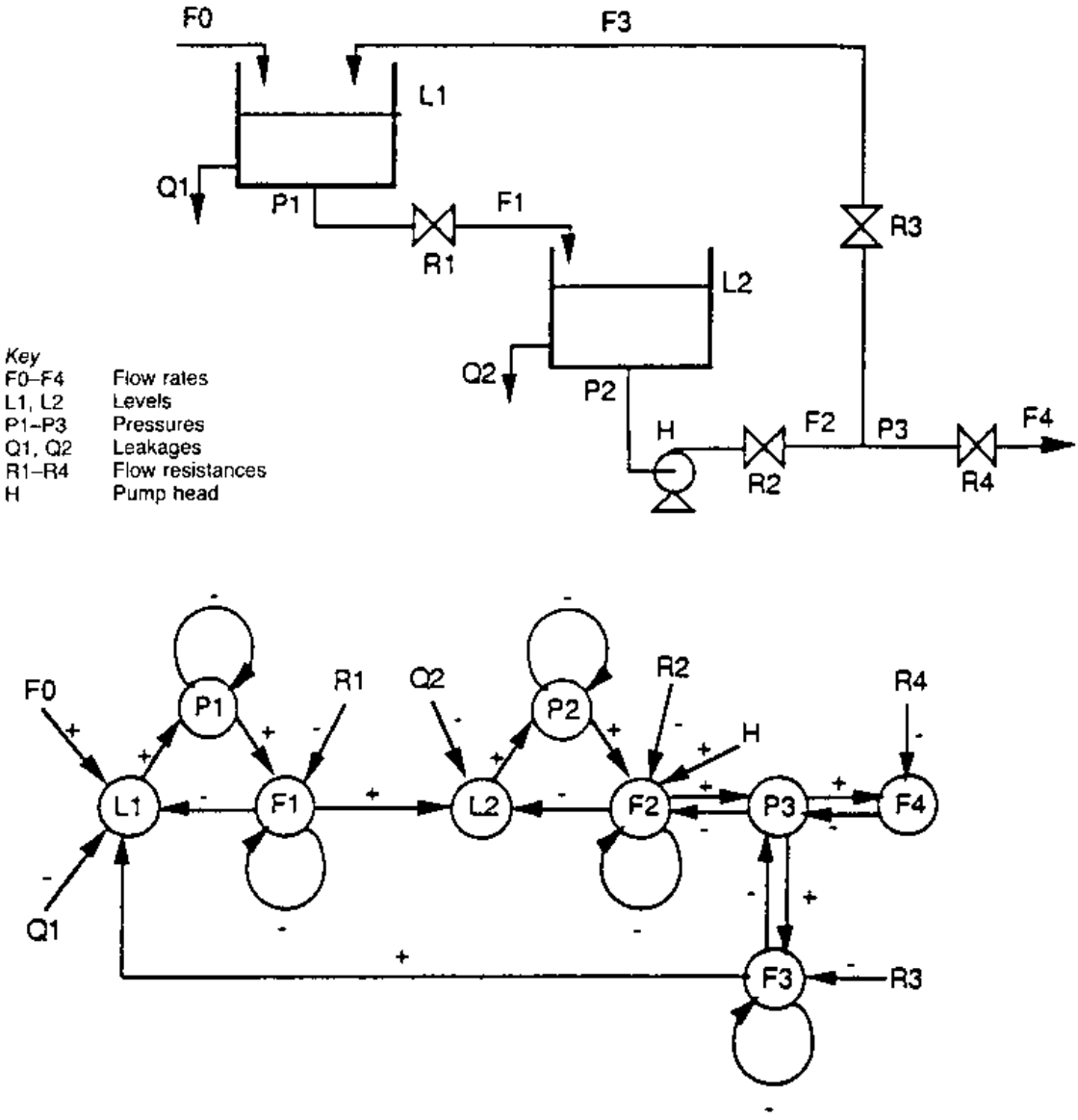


Figure 30.12 *A recycle tank system (Fanti, Chung and Rushton, 1993: after P. Rose and Kramer, 1991) (Courtesy of the Institution of Chemical Engineers)*

30.36.7 Ambiguities and loops

Fault propagation deals with the deviations of process parameters but the degree of deviation is not fully defined. In consequence, ambiguities arise. A particular disturbance may apparently give rise to a number of possible alternative responses or interpretations. The problems caused by ambiguities have been discussed by Waters and Ponton (1989).

These ambiguities may arise when faults are being propagated forward from an event, as in an event tree, or backward from an event, as in a fault tree. In either case rules are required for the resolution of the ambiguities. Unresolved parameters also occur due to the presence of loops and recycles. Some of the options for resolution are discussed by Waters and Ponton.

One approach to such resolution is to introduce additional constraints. Work on these lines for digraphs has been described by P. Rose and Kramer (1991), and developed further by Fanti, Chung and Rushton (1993). The digraph representing a process flow structure usually contains loops, there is more than one path which can be traced between nodes and, since the paths may have opposing influences, ambiguities arise. The approach taken by Fanti, Chung and Rushton is the use of high level constraints such as a mass balance. They illustrate their method using the recycle tank system of

Table 30.14 *Response of recycle tank system (after Fanti, Chung and Rushton, 1993) (Courtesy of the Institution of Chemical Engineers)*

A Initial candidate responses

Disturbance	*Responses*							
	L1	*F1*	*L2*	*F2*	*P3*	*F3*	*F4*	
R3 +	−	−	−	−	−	−	−	Candidate R3A
	−	−	−	−	0	−	0	Candidate R3B
	−	−	+	−	+	−	+	Candidate R3C
	−	−	0	−	+	−	+	Candidate R3D
	−	−	−	−	+	−	+	Candidate R3E
R4 +	+	+	+	+	+	+	+	Candidate R4A
	+	+	+	+	+	+	0	Candidate R4B
	+	+	+	+	+	+	−	Candidate R4C

B Responses after resolution

Disturbance	*Responses*							
	L1	*F1*	*L2*	*F2*	*P3*	*F3*	*F4*	
R3 +	−	−	−	−	0	−	0	Candidate R3B
R4 +	+	+	+	+	+	+	0	Candidate R4B

The supporting argument is as follows. Disturbances R3 + and R4 + each leave F0 unchanged, F0 = 0. Overall mass balance requires F4 = F0. Hence candidate responses R3A, R3C, R3D and R3E and responses R4A and R4C are eliminated.

P. Rose and Kramer shown in Figure 30.12, which also gives the corresponding digraph. Their results for this problem are shown in Table 30.14. Section A of the table shows the possible responses of the variables flow F1–F4, level L1–L2 and pressure P3 to changes in valve resistance R3 and R4. Five interpretations are identified. Section B of the table shows the resolution of these ambiguities using high level constraints.

Another approach is the use of heuristics. An example is furnished by the work of A. Hunt *et al.* (1993e) on fault tree synthesis. A configuration which is liable to give rise to such inconsistencies is a unit with more than two ports. Inconsistencies arise from looping around the unit. In this case use is made of the rule that in the development of the tree at a particular unit only one change of port is allowed.

Although ambiguities and loops undoubtedly present problems and merit further work, they do not appear to have proved a serious hindrance to the development of fault propagation tools for tasks such as hazard identification or fault tree synthesis.

30.36.8 Structure identification

Another problem which arises in modelling for fault propagation is that of identifying structural features in the flow diagram. The structural feature in question may be: a recycle flow; a control loop and the streams affected by its action; a trip loop and the streams affected by its action, whether it be a loop with an open or a closed trip valve; or a divider-header combination, where the divider and the header may be separated by a number of intermediate units, and where there may be a number of dividers and headers nested or staggered.

Some types of structural information are readily provided by the user, and in this case this may be the appropriate course. In other cases it is not easy for the user to identify the structure, but it is feasible to devise an algorithm to identify it, in which case this may be the best approach.

In any event, the identification of structure is a generic problem. Approaches to the problem have been described in a number of different areas, e.g. heat exchanger networks (Pethe, Singh and Knopf, 1989); and fault tree synthesis (A. Hunt *et al.*, 1993a–e).

30.36.9 Alternative representations

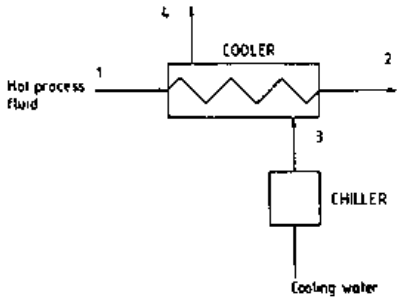
As already indicated, fault propagation relations may be represented in a number of different ways. To some extent at least it is possible to map between them. An account of alternative representations and of mapping has been given by Aldersey, Lees and Rushton (1991).

Some forms of representation available include (1) functional equations, (2) program rules, (3) digraphs, (4) block diagrams, (5) logical expressions, (6) truth tables, (7) cut sets, (8) fault trees, and (9) event trees.

Figure 30.13 shows a heat exchanger system together with representations of the system in the nine forms just listed. The heat exchanger is a cooler in which a hot process fluid is cooled by cooling water. The cooling water is itself cooled by a chiller prior to entering the main cooler.

Of the three graphical forms, the digraph contains the most information. For a particular event, a fault tree or an event tree may be obtained from the digraph, but with loss of information.

A common method of constructing a fault tree is to start with a digraph and to obtain the required fault tree from it. Accounts of this approach have been given by Lapp and Powers (1977a,b), Lambert (1979) and Andrews and Morgan (1986).



(a)

Functional equations

$Q_2 = f(Q_1)$

$Q_4 = f(Q_3)$

$T_2 = f(Q_1, -Q_3, T_1, T_3)$

$T_4 = f(Q_1, -Q_3, T_1, T_3)$

Event statement

EF: T_2 HI, T_4 HI

(b)

Program rules

for fault propagation

rule (pipe, propagation, [q,2], [q,1], [ ])

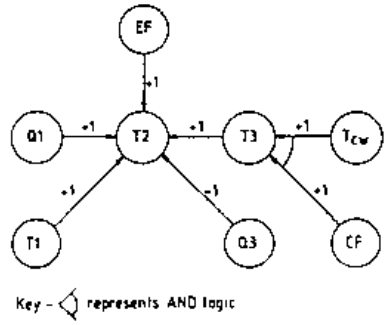
(see first functional equation in (b) above; other rules not given)

for fault initiation

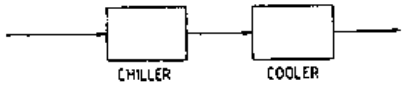
rule (pipe, environment, [['external fire', ' ', ' ']][[t,2,hi]])

(see event statement in (b) above)

(c)



(d)



(e)

Logical expressions

T_2 HI = Q_1 HI + Q_3 LO + T_1 HI + T_3 HI + $\dot{EF}$

T_3 HI = (T_{cw} HI) (CF)

(f)

T2 HI	Q1 HI	Q3 LO	T1 HI	EF	T3 HI
T	T	F	F	F	F
T	F	T	F	F	F
T	F	F	T	F	F
T	F	F	F	T	F
T	F	F	F	F	T

(partial table only, contains only lines where T_2 HI is true)

T3 HI	T_{cw} HI	CF
T	T	T
F	T	F
F	F	T
F	F	F

(full table)

(g)

Figure 30.13 *Some forms of representation of a process system and of faults in such a system (Aldersey, Lees and Rushton, 1991): (a) cooler system; (b) functional equations and event statements (EF, external fire); (c) program rules (in Prolog); (d) digraph (CF, cooler failure); (e) block diagram for event Q4 LO (LO, low); (f) logical expressions for events T_2 HI and T_3 HI (HI, high); (g) truth tables for these same events (F, false; T, true); (h) minimum cut sets for event T_2 HI; (i) fault tree for event T_2 HI; (j) event tree for event T_{CW} HI (Courtesy of the Institution of Chemical Engineers)*

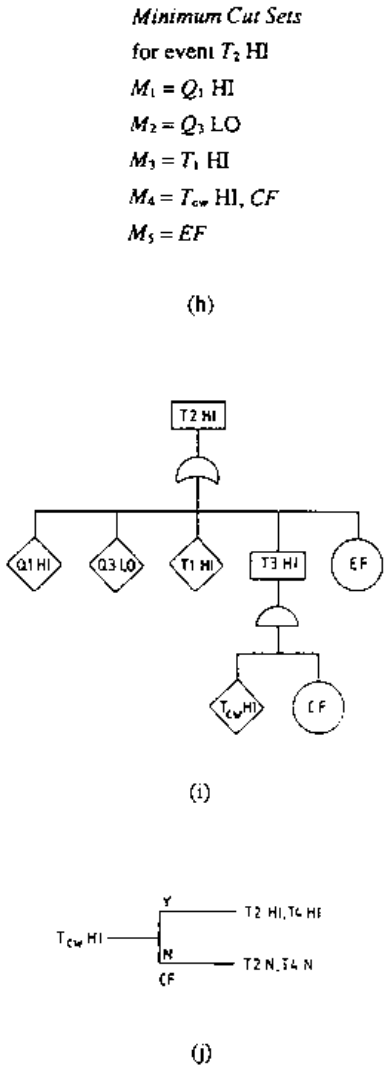


Figure 30.13 *continued*

Mapping between fault trees and event trees, and vice versa, has been described by Aldersey, Lees and Rushton (1991).

There are now a considerable number of mathematical models of process plant and it may be desired to derive a qualitative model from an existing quantitative model.

A method of doing this was developed by Andow (1973) in his work on modelling for alarm diagnosis. Consider the relationship

$$\underset{6}{\text{RHS}} = \underset{6}{\text{A}} + \underset{5}{\text{B}} * ((\underset{2}{\text{C}} + \underset{1}{\text{D}}/\underset{3}{\text{E}}) - \underset{4}{\text{F}}) \uparrow \underset{\ }{\text{G}} \qquad [30.36.8]$$

where RHS represents the right-hand side of an equation and the numbers show the order of evaluation following the normal rules of algebra. It can be seen that evaluation does not occur in the order in which the operators are discovered. Converted to Reverse Polish Notation the relation becomes

$$\underset{1\ 2\ \ 3\ \ 4\ 5\ 6}{\text{RHS} = \text{A B C D E} / + \text{F} - \text{G} \uparrow * +} \qquad [30.36.9]$$

The operators are now in the correct order, whilst the operands remain in their original order.

This use of this technique to reduce quantitative models to qualitative ones is described by Andow, who gives full details of the transformation.

30.36.10 Generic modelling

Fault propagation modelling may be used to support a range of safety-related techniques such as hazard identification, fault tree synthesis, operating procedure synthesis and alarm diagnosis. There is clearly an advantage to be gained by formulating a type of generic model which supports all these methodologies and others. On the other hand, the development of a particular technique should not be unduly constrained by the requirement for commonality. This is illustrated in the work of Lees, Rushton, Chung and co-workers. The models used in early development of particular techniques differed slightly, but a considerable commonality was retained which is built on in the later work.

30.36.11 QUEEN

A code QUEEN, designed to provide a front-end for fault propagation modelling in activities such as hazard identification, fault tree synthesis, operating procedure synthesis and alarm diagnosis has been described by Chung (1993).

30.37 Hazard identification

In addition to computer aiding of process synthesis and plant design in general, there are a number of types of aid which specifically address hazard and safety issues. Qualitative modelling, and particularly fault propagation modelling, is an important feature in many of these aids.

The first form of computer aid considered here is aids for the identification of hazards. A number of workers have described systems which perform functions broadly similar to those carried out in a hazard and operability, or hazop, study or which serve as an aid in the conduct of a study of this general type. Systems include: HAZID by Parmar and Lees (1987a,b); a system described by Weatherill and Cameron (1988, 1989); HAZOPEX by Heino, Suokas and Karvonen (1989a,b) and Suokas, Heino and Karvonen (1990); HAZEXPERT by Goring and Schecker (1992); and COMHAZOP by Rootsaert and Harrington (1992).

The applicability of AI techniques in the this area is discussed by Ferguson and Andow (1986). The identification of hazards is in many ways one of the least promising fields for computer methods. It is very difficult to devise a technique which can compete with man's ability to think laterally and to make apparently obscure connections.

Before describing specific systems there are some general points which need to be made about hazop-type aids. The first concerns the use to which such an aid might be put. Workers in the field generally recognize the power of the current hazop method and are cautious about suggesting that aids under development might supplant it. Usually it is suggested that such an aid is likely to find use during the design and prior to the hazop study.

Work in this area has highlighted the fact that in some instances the defect identified is that the design fails to conform to some aspect of company good practice. Typically this is a failure to incorporate some feature in standard equipment such as a pump set or a storage tank. It may be preferable to handle deficiencies of this sort by some means other than a hazop-type approach, such as a checklist, an archetype design, and so on. In other words, the hazop study should not have to concern itself with this sort of defect.

There is scope for the development of computer-based screening tools, or design advisers, to perform these functions before the design is subject to hazop-style review, whether manual or computer-aided. An important feature of a system is the degree of interaction between the user and the program. Some aids are highly interactive, others are not. However, even where the aid is interactive, its intended use is generally prior to rather than during the hazop study.

Another issue concerns the input of the information needed by the computer aid. This generally consists as a minimum of the set of process units and the connections between them. In some systems considerably more information may be required. The information input may therefore constitute an appreciable overhead in the use of the method. Thus it is attractive to capture this information from the computer aided design (CAD) system. In current systems this may not be a trivial matter.

With regard to the general structure of hazard identification aids, the trend is to follow the method used in conventional hazop studies, in which the examination moves systematically through the plant line by line and considers in turn for each of the principal process variables the potential deviations, their causes and consequences. The adoption of this approach appears to be attributable less to an intention to mimic the hazop process than to a recognition that the procedure followed seems as effective as any in ensuring a high degree of completeness in the identification.

Although the hazop study is now perhaps the most widely recognized aid to hazard identification, it should not be forgotten that the fault tree is also a powerful tool, not just for quantifying the frequency but also for identifying the existence of hazards. As described later, considerable progress has been made in the computer aiding of work on fault trees.

An account is now given of some of the systems which have been developed for the computer aiding of hazard identification. Interestingly, there are a number of quite different approaches.

30.37.1 HAZID

A research computer code HAZID for hazard identification on continuous plants has been described by Parmar and Lees (1987a,b). HAZID is based on the fault propagation approach outlined in Section 30.36. The plant configuration is entered and unit models are assigned to the units. These unit models consist of fault propagation rules and are held in a model library. Each unit is examined in turn to identify undesirable consequences and, using fault propagation, their causes. The program is written in FORTRAN with the inference engine in Prolog and is non-interactive. A more detailed account of HAZID is given Section 30.38.

30.37.2 Weatherill and Cameron system

A prototype expert system for hazard identification has been described by Weatherill and Cameron (1988, 1989). The system, which is highly interactive, is used to examine the system line by line. The user enters for each line the identification of the process units to which it is connected and of the fittings in the line. A deviation is treated as a goal, the existence of which the system attempts to prove by interrogating the knowledge base to identify possible causes. The knowledge base contains facts and rules structured around the units rather than around the deviations. The program is written in Prolog.

30.37.3 HAZOPEX

Another prototype expert system for hazard identification is HAZOPEX, which is described by Heino, Karvonen Suokas and co-workers (Karvonen, Suokas and Heino, 1987; Heino, Suokas and Karvonen, 1989a,b; Suokas, Heino and Karvonen, 1990; Heikkila and Heino, 1992; Heino, Poucet and Suokas, 1992).

HAZOPEX is a highly interactive tool. The plant topology is loaded at the start using a model editor. The user then examines the plant line by line.

The knowledge base is organized as a hierarchy of units, with classes and subclasses, and with inheritance of characteristics. Search may be carried out at two levels. For a general level search rules are classified by deviation type and for a lower level search by unit type. The level of search is controlled by the user.

One characteristic feature of HAZOPEX is that, whereas other systems use detailed models of the different units, it uses instead rather generalized tank and line models. Another feature is that the equipment models are complemented by a relatively well developed fluid model.

Sets of rules are applied for deviations, consequences and countermeasures. The number of rules used is: for causes, 330 rules; for consequences, 20 rules; and for countermeasures, 20 rules. Thus most of the rules relate to the causes. Less effort has been put into the development of rules for consequences and countermeasures, which are more dependent on the specific process.

Various types of display are used to show the output generated. One gives the results in tabular form, akin to the output from a conventional hazop study. Another shows a deviation at the centre with two trees attached, the causes tree being structured rather like a fault tree and a consequences tree like an event tree.

The project has involved a process of continuous evaluation, which is regarded as having an important role in prototype development. The authors describe work done to validate the program using an ammonia storage tank system and comparing the results obtained

with those from a conventional hazop study. They also give an account of an application session.

HAZOPEX has been developed using a LISP machine and an expert system shell.

30.37.4 COMHAZOP

The COMHAZOP system is described by Rootsaert and Harrington (1992). The plant configuration is entered and unit models are assigned to the units. The program examines deviations associated with the units and uses rules to identify the causes of these deviations.

30.37.5 HAZEXPERT

Goring and Schecker (1992) describe the hazard identification system HAZEXPERT. This aid eschews a hazop-style approach. The plant configuration is entered. A set of pre-defined consequences such as overpressure, explosion, etc., is used. A search, limited in scope around the set of units under examination, is conducted to discover the causes of these events. The program contains a generic hazard knowledge base in which a key concept is disturbance of the mass or energy balance. HAZEXPERT is implemented using an expert system shell.

30.37.6 PSAIS

PSAIS (Plant Safety AI System) is described by Schönenburg (1992). The program utilizes only a limited number of rules but holds a large collection of design cases. Examination of a plant design is based on accessing 'similar' cases in the design case database. If no similar case is found, a new case is created. Use is made of fuzzy matching. In this way PSAIS benefits from a continuous process of learning.

30.37.7 HAZExpert

The HAZExpert system is described by Venkatasubramanian and Vaidhyanathan (1994). The general approach described appears broadly similar to that used in HAZID. The authors identify as distinguishing characteristics an emphasis on consequences and the resolution of ambiguities. HAZExpert is implemented in G2 by Gensim (1992).

30.38 Hazard identification: HAZID

A more detailed account is now given of one particular code for hazard identification. This is the HAZID code described by Parmar and Lees (19876a,b). The method follows closely the general approach taken in a hazop study, but draws on generic fault propagation technology developed for fault tree synthesis. An overview is now given of HAZID, which both illustrates an application of fault propagation modelling and serves as an example of a hazard identification code.

30.38.1 Hazard identification strategy

Initially the problem of hazard identification was approached without any preconception as to the structure of the method. Both top-down and bottom-up approaches used in fault trees and event trees, respectively, were considered as possible candidates. Completeness in the identification of hazards is the crucial feature of an effective method. A top-down method must therefore start from a complete list of consequences and a bottom-up method from a complete list of causes. It is difficult to provide lists which ensure completeness in all situations. In a conventional hazop the starting point is the list of process parameters in a pipe and the list of guidewords. This pair of lists yields a closed set of events but generates an open set of causes and consequences. This characteristic of the hazop approach is the desired one and was therefore adopted for the computer aided method also.

30.38.2 System decomposition

The starting point for the method is the piping and instrument diagram. This is then converted to a block diagram. As in a conventional hazop the analysis is carried out on the pipes rather than the vessels. The block diagram contains the vessels and other major items, but most of the elements in it are pipework items such as pumps, hand valves, control loops, etc. For each unit in the block diagram a unit model is specified, drawing on a library of unit models. Additional models may be configured by the user and entered in the library as required.

30.38.3 Unit models

A unit model is a representation of the propagation of input parameter deviations into output parameter deviations and also of the initiation and termination of these deviations. The fault propagation utilizes the methodology described in Section 30.36. The basic representations used are (1) propagation equations and (2) event statements.

For specific applications it may be convenient to transform these basic representations into alternative forms. Thus in fault tree work they may be converted to a set of mini-fault trees. In HAZID they are converted into a set of rules written in Prolog.

The initial and terminal events are, respectively, the causes and consequences which the hazard identification procedure seeks to discover. The completeness of the identification depends on the quality of the modelling of these events.

The configuration of the unit models is guided by the use of the following checklist for the initial event statements:

(1) function;
(2) hydraulics;
(3) containment;
(4) impurities;
(5) environment.

A process unit has a particular function. For example, it is the function of a gas absorption column to absorb a solute from a gas stream into a liquid stream. Thus one function fault in such a unit is that maldistribution of the liquid causes the outlet gas solute concentration to be high and the outlet liquid solute concentration low. This may be represented by the initial event statement

maldistribution $> x_2$ hi, x_4 lo

where x is the concentration of the solute and subscripts 2 and 4 refer to the outlet gas and outlet liquid streams, respectively. This is equivalent to the rule that if maldistribution occurs, then x_2 hi and x_4 lo may occur.

A process unit has a hydraulic function in that it should transmit flow, and a containment function, in that it should not leak. It also has functions related to impurities and its environment in that it should not introduce impurities and should not undergo excessive deviations due to environmental changes. Typical initial event statements for various units for these other four functions respectively are:

blockage $> q_1$ none, q_2 none
leak (major) $> qi$ hi, q_2 lo
broken packing $> ia_4$
external cold source $> t_2$ lo

where i is the impurity concentration, q is the, flow t is the temperature and a is the impurity packing debris.

Terminal event statements usually relate to a serious excursion of a process parameter. Some typical terminal event statements are

p_2 hi $>$ overpressure
t_2 lo $>$ undertemperature
l_4 hi $>$ overfilling

where l is the level, p is the pressure and t is the temperature.

Initial and terminal event statements provide the means of entering a fairly comprehensive list of initial and terminal events, and hence causes and consequences.

30.38.4 Fluid and materials models

In addition to the unit models there are models for the process fluids and for the materials of construction. These are used primarily to allow consequences to be made conditional on the existence of a particular process fluid or material of construction susceptibility. For example, low flow may cause blockage, but only if the process fluid contains solids which can deposit out; low temperature may cause brittle fracture, but only if the material of construction is mild steel.

There are special treatments for the common faults leak and blockage, and releases to the environment are consolidated in a special escape model.

30.38.5 Cause and consequence generation

The hazard identifier program receives as input tables giving the configuration of the block diagram and listing the library models to be used for each unit. The program operates on the system line by line. For a given line each parameter deviation is examined in turn and its causes and consequences are generated from the initial and terminal event statements in the unit models.

The link between the causes and consequences listed for a particular parameter deviation is the deviation itself. In general, most of the causes result in most of the consequences and most of the consequences result from most of the causes, but not all. For example, in a pump delivery shut in is a cause of no flow and results in the consequences pump overheats and loss of level in the downstream vessel, but no changeover to a stand-by pump is a cause of no flow and results in loss of level but not in pump overheating.

With regard to the direction of search for causes and consequences, Figure 30.14 shows two options. In Method 1 the search is from local cause to distant causes, whilst in Method 2 it is from local consequence to distant consequences. HAZID uses Method 1, for two reasons. First, this method involves the evaluation of consequences rather than causes and such an evaluation is considered the prime form of filtering. Second, the method allows the possibility of tracing a consequence linked to a number of causes and is compatible with the search for such causes using a fault tree.

30.38.6 Screening of faults

In the foregoing, attention has been focused on the generation of potential faults. In the absence of some screening mechanism the number of faults generated can be very large. This is a common problem in computer-generated output, but it occurs to a degree in conventional hazop also. Several approaches may be taken. The main distinction is between suppression of the initial generation of the faults and handling of faults after they have been generated.

A particular form of suppression is effected by the fluid and materials of construction models, as already described. In many cases a fault thrown up by the fault propagation modelling has a credible realization only if there is a particular fluid susceptibility, so that where the fluid model contains no such susceptibility, the fault need not be generated. Similar considerations apply to the materials of construction model.

With regard to handling of faults after generation, mention has already been made of the consolidation of similar faults caused by different items in a single line.

The other methods of handling faults involve some form of screening. The simplest approach here is to lay 'masks' over the output. A variety of types of mask may be used for different purposes. A hierarchy of masks may be used which give successively larger amounts of detail. Other specialist masks may be envisaged for particular problem areas.

Another more difficult but worthwhile form of screening is the use of engineering heuristics to evaluate faults. The evaluation may address causes or consequences. Suitable heuristics are of various types, but in each case the purpose is to assist the decision as to whether a fault can be disregarded either because the cause is not credible or the consequence is negligible. Some heuristics relate to the frequency and cost of faults, and require both estimated values and cut-off levels. Other heuristics are based on engineering practices. For example, there are usually company practices which determine whether in a given case a liquid relief valve is provided on a section of pipe which is shut in.

30.38.7 Fault consolidation

For the lines connecting the vessels and other major equipment, use is made of a special pipe model. Faults in the line due to minor units such as pumps, hand valves and control loops are collected up and consolidated so as to avoid excessive proliferation of faults. In this way a fault such as a blockage is flagged in the line only once, but all the causes of the fault are identified.

30.38.8 Model generation and model library

The configuration of a unit model is carried out using a model generation program. The data are entered on a proforma. A typical proforma is shown in Figure 30.15.

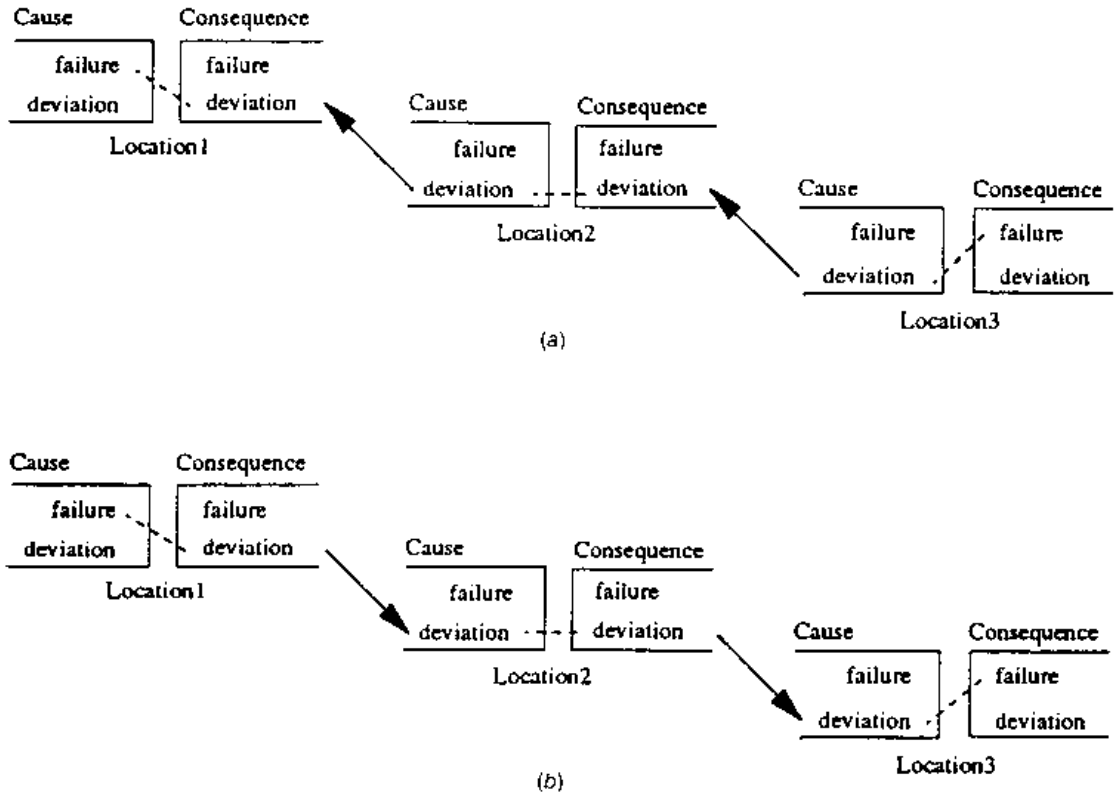


Figure 30.14 *HAZID: generation of causes and consequences (Zerkani and Rushton, 1992): (a) search for causes; (b) search for consequences (Courtesy of Pergamon Press)*

Items 1–6 are entered by the user and the remaining items are generated by the program. The rules in items 7–9 are in Prolog, as described below.

Models are held in a model library. In some applications the user may find all the models required already in the library. Where this is not so, he configures the missing models using the model generation program.

There are certain relationships between models which may be exploited to achieve a degree of automatic model generation. One is the hierarchical structure of models. Thus a pump is a subclass of the class of pressure raisers and inherits certain characteristics. Even where there is no formal hierarchy, a group of models may be related by some shared process or feature. In such cases use may be made of model archetypes, or partial models.

Much modelling centres around ports at the inlet and outlet of vessels and other equipment. A taxonomy of standard ports permits the selection of appropriate sets of equations, or models, for such ports.

30.38.9 Computer codes

The main programs in the HAZID package are: MASTER, which does the housekeeping; CONFIGURATOR, which handles the configuration; IDENTIFIER, which is the core program and generates the cause and consequence lists for the parameter deviations; CONSOLIDATOR, which turns these lists into a table similar in form to that produced by a conventional hazop; and MODGEN, which generates the unit models. There is a unit model library. The task of IDENTIFIER is to handle rules and the program is written in Prolog. The other programs are written in Fortran.

30.38.10 Illustrative example: water separator

An illustrative example of the use of HAZID has been given by Parmar and Lees (1987b). The plant examined is the feed section of the alkene dimerization plant described by Lawley and shown in Figure 8.25. The corresponding block diagram for this plant is shown in Figure 30.16. Table 30.15 gives part of the hazard identification table generated for this example together with extracts from the original table of Lawley, which was given in Table 8.29.

30.39 Hazard Identification: Enhancements

The published work on computer-based aids for hazard identification suggests that there is still much to be done to devise an aid which is useful in identifying hazards

1. Model number, name
   13 pipe
   1 2
2. Engineering description and assumptions
   Engineering description
   N/A
   Engineering assumptions
   N/A
3. Propagation equations
   $p_2 = f(p_1)$
   $q_2 = f(q_1)$
   $t_2 = f(t_1)$
   $x_2 = f(x_1)$
4. Supplementary information
   Normal state: N/A
   No multicomponent features
   Failure modes: 1
5. Initial event statements
   blockage > q_2 lo, q_2 none, p_1 hi
   leak > escape
   leak (rupture) > q, hi, q_2 lo, q_2 none, p_2 lo
   external cold source, cold weather, lagging loss > t_2 lo
   external heat source, lagging loss, fire > t_2 hi
   external heat source with blocked-in pipe > p_2 hi
6. Terminal events
   p_2 hi > leak (rupture)
   t_2 lo > leak (rupture)
7. Rules for fault propagation
   rule (pipe, propagation, [p, 2], [[p, 1]], [ ])
   rule (pipe, propagation, [q, 2], [[q, 1]], [ ])
   rule (pipe, propagation, [t, 2], [[t, 1]], [ ])
   rule (pipe, propagation, [x, 2], [[x, 1]], [ ])
8. Rules for fault initiation
   rule (pipe, hydraulic, [['blockage', ' ', ' ']], [[q, 2, lo], [q, 2, none], [p, 1, hi]])
   rule (pipe, containment, [['leak', ' ', ' ']], [['escape', ' ', ' ']])
   rule (pipe, containment, [['leak (rupture)', ' ', ' ']], [[q, 1, hi], [q, 2, lo], [q, 2, none], [p, 2, lo], ['escape ' ', ' ']])
   rule (pipe, environment, [['cold weather', ' ', ' '], ['lagging loss', ' ', ' ']], [[t, 2, lo]])
   rule (pipe, environment, [['hot weather', ' ', ' '], ['lagging loss', ' ', ' '], ['fire', ' ', ' ']][[t, 2, hi]])
   rule (pipe, environment, [['external heat source with blocked-in pipe', ' ', ' ']], [[p, 2, hi]])
9. Rules for fault termination
   rule (pipe, effect, [[p, 2, hi]], [['leak (rupture)', ' ', ' ']])
   rule (pipe, effect, [[t, 2, lo]], [['leak (rupture)', ' ', ' ']])
10. Model status:
    Written: JCParmar June 1986
    Checked: FPLees June 1986
    Usage: 3 Configurations

Figure 30.15 *HAZID: proforma for configuration of a unit model (Parmar and Lees, 1987b) (Courtesy of Elsevier Science Publishers)*

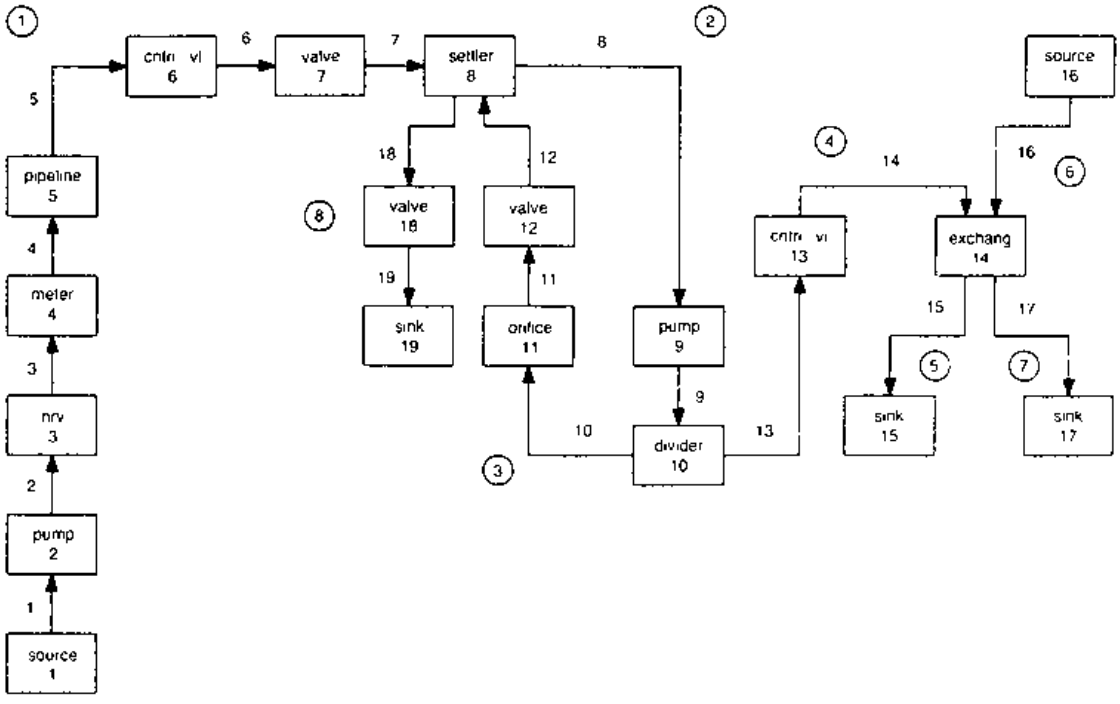


Figure 30.16 *HAZID: illustrative example: block diagram for alkenes dimerization plant (Parmar and Lees, 1987b) (Courtesy of Elsevier Science Publishers)*

prior to conventional hazop, let alone one which might do more than this.

The current state of the art may be summarized by saying that, in general, aids are more successful in identifying causes than consequences, the range of which tends to be rather limited, and both are lacking in richness and are thus rather stereotyped. The overheads for the input of data tend to be too high. The output tends to be lacking in discrimination, and thus excessive.

An aid such as HAZID is built largely around fault propagation, which utilizes models based on engineering principles and which is stronger on the identification than on the evaluation of faults. Fault generation needs to be enhanced by grafting onto this basic mechanism domain expertise. Thus, for example, a heat exchanger may have expertise bearing on tube vibration under abnormal flow conditions, blockage under no flow conditions, pinhole leaks between tubes and the shell, the overpressure hazard following tube burst, the need for space to remove the tube bundle, and so on. Perhaps even more important is the need to strengthen fault evaluation. There are various methods of doing this but most may be broadly classed as forms of expertise.

Features in which enhancement of current methods is likely to be of value include the following: (1) design screening, (2) information acquisition, (3) generation of faults, (4) evaluation of faults and (5) presentation of output.

30.39.1 Design advice and screening tools

The point has already been made that if the designs coming forward incorporate defects which are relatively elementary and numerous, a hazop-style aid may not be the most efficient way of correcting the situation. There may be scope for assisting the designer by providing a design advisor tool. Such a tool is essentially an aid to design synthesis. Likewise, it may be appropriate to provide a design screening tool to filter out certain common and readily identifiable defects. In contrast to the design advice tool, this is a tool for design analysis.

A design screening tool is likely to rely largely on an examination of the configuration of the units and of the plant as a whole. Configuration screening is discussed further below. Suffice it to say that it needs to be catered for somehow and that, if it is not performed by a separate aid, it is necessary to incorporate it in the main hazard identification aid.

30.39.2 System discipline

It can be envisioned that over time aids such as those for representing design issues described earlier and the hazard identification aids described here could exert a significant influence on the design process. Such aids tend to require adherence to a more formal discipline involving a more explicit declaration of issues, arguments and intent. This is not only a condition for the effective

Table 30.15 *HAZID: illustrative example; hazard identification table generated for alkene dimerization plant (Parmar and Lees, 1987b) (Courtesy of Elsevier Science Publishers)*

Process deviation	*Original hazop causes*	*Computer-aided hazard identification causes*	*Original hazop consequences*	*Computer-aided hazard identification consequences*
No flow	No hydrocarbon at intermediate storage	Source: q_1 none source empty	Loss of feed to reaction section and reduced output. Polymer formed in heat exchanger under no flow conditions	Pump: Pump fluid overheats Settler: q_1 none Outflow(s) none l_5 none
	J1 pump fails (motor fault, loss of drive, impeller corroded away, etc.)	Pipe: Blockage Leak (major) Pump: Loss of NPSH Rotation fault Impeller fault Cavitation Low b.pt. material gassy material	J1 pump overheats	
	Line blockage, isolation valve closed in error or LCV fails shut	Delivery shut in No change to stand-by Stand-by fail on demand Maloperation of valves Blockage Leak (major) NRV: Valve stuck closed Pipeline: Blockage Leak (major) Control valve: Loop fails closed Sensor fails closed Controller fails closed Control valve fails closed Set point moved closed Isolation valve closed Valves: Valve moved closed	Hydrocarbon discharged into area adjacent to public highway	
	Line fracture			
More flow	LCV fails to open or LCV bypass open in error	Source: q_1 high Meter: Bypass fails Bypass moved open Control valve: Loop fails open Sensor fails open Controller fails open Control valve fails open Set point moved open Bypass directed open	Settling tank overfills Incomplete separation of water phase in tank, leading to problems in reaction section	Meter: Inaccurate measurement Settler: q_1 high poor settling i_{a-2} high l_5 high Liquid enters vent
Less flow	Leaking flange or valved stub not blanked and leaking	Source: *pi pl* q_1 low Blockage Leak (major) Pump: Loss of NPSH Rotation fault Impeller fault Cavitation Low b. pt. material Gassy material Delivery part shut Blockage Leak (major) NRV: Valve fails part closed Pipeline: Blockage Leak (major) Control valve: Loop fails part closed Sensor fails part closed Controller fails part closed Control valve fails part closed Set point moved part closed Isolation valve part closed Blockage Valve: Valve partly closed	Material loss adjacent to public highway	Meter: Inaccurate measurement Settler: q_1 low Outflow(s) low l_5 low

LCV, level control valve; NPSH, net positive suction head; NRV, non-return valve.

integration and exploitation of these aids but also a desirable development in the design process itself.

Permitted terminology
One aspect of this is the discipline to be adhered to in the terminology used. It is good practice to use lists of the permitted terminology for units, faults, process variables, deviations and so on.

As a simple example, confusion can be caused if the state of a valve is described on some occasions as 'closed' and on others as 'shut'. More fundamentally, the discipline is of value with respect to generic and specific faults and to the inheritance of faults. Thus, for example, use might be made of the generic faults 'block', indicating complete blockage, and 'outflow', indicating major leak. Realizations of the generic fault block in a line might be the specific faults blockage, closure of valve, freezing of fluid or polymerization of fluid.

30.39.3 Fault generation and evaluation

As already stated, a hazard identification aid is required both to generate faults and to evaluate them. Fault generation is primarily by means of fault propagation models, fluid and materials of construction models, and expert rules. The prime means for fault evaluation are the fluid model and expert rules.

30.39.4 Integration of expertise

The generation of faults is done partly by fault propagation, but to achieve a greater richness and completeness it is necessary to introduce in addition various forms of expertise. The following are some of the attachment points, or 'hooks' to which such expert rules may be attached: guidewords; faults; deviations; undesired outcomes; units; lines; configuration of units (including connectivities and elevations); fluids; reactions; impurities and their sources; materials of construction; pressure raisers (pumps, compressors); instrumentation; control computers; protective devices (especially relief valves); small items (drain and sample valves, filters, small bore pipework, etc.); mode of operation (batch, continuous, etc.); operations (usual modes of operation, operating instructions); maintenance; storage; transport; utilities; environmental influences (heat, cold, rain, extreme weather); and environmental impacts (releases).

Expert rules are also a prime means for the evaluation of faults. Once a fault has been generated, any expertise available to the program can be brought to bear to evaluate it. This applies whether the fault generation step has involved fault propagation, the fluid model or fault generation expertise. Often, fault generation and evaluation will be part of the same package of expert rules.

30.39.5 Information requirements

The hazard identification activity requires the availability of a considerable amount of information. The information requirements for conventional hazop have been discussed in Chapter 8.

Minimal requirements for a computer aid are generally (1) the piping and instrument diagram, and information about (2) the main plant units, (3) the fluids and (4) the materials of construction. In addition, however, information may be needed about other aspects such as design intent and operating procedures.

Some comments are now given about some of these types of information.

Fluids
Information is required about the properties of the fluids in the plant. This is discussed in more detail below. Suffice it to say at this point that in large part this is information about fluid properties and susceptibilities. The former should be available in the standard generic fluid properties data bases but much of the latter may not.

Materials of construction
Information is also required on the properties of the materials in the plant, essentially on their susceptibilities. Provision of this information is the function of a generic materials of construction database.

Design intent
There is a quite large amount of information on design intent which is not necessarily given in the piping and instrument diagram (P&ID).

This category covers a wide range of types of information. One type may be broadly characterized as configurational information. For example, the P&ID may show two pumps piped up in parallel without making it clear whether these are 50% or 100% pumps. Or, again, two pressure relief valves may be shown but with no indication on setting, capacity or stagger. Another category is that which relates to the function of the unit, especially where this involves a dual or subsidiary function or a constraint on function.

Operating procedures
Another important category of information is the operating procedures. Ideally these should be available at the time where the hazard identification is undertaken, but they may well not be.

Resident hazards
It is commonly the case in a conventional hazop that even before the study is commenced the team already knows that the plant is subject to certain hazards, or other problems. In conducting the examination these 'resident hazards' are uppermost in the mind. It makes sense in devising a computer method to find some way of ensuring that the search covers such resident hazards.

Information representation
For some types of information the form of representation appears straightforward. For fluid–materials incompatibilities, for example, a look-up table is a natural format. Moreover, such information is of the type which should in large part be available in standard databases. With other types of information, such as design intent or operating procedures, there are issues both as to the representation most useful to the hazard identification aid and as to the ease of acquisition.

Lack of information: effects and strategies
Lack of information has certain consequences. In some cases the system may fail to generate a fault. More often,

it will be unable to evaluate a potential fault which it has identified. There are strategies for coping with a lack of information. One is to conduct a dummy run of the hazard identification aid to establish the information which is missing. This implies that the data are to be provided prior to the main run.

An alternative approach is to use default assumptions about matters such as design intent or operator procedures. It can be envisaged, for example, that for many standard operations a corresponding standard, default operating procedure is attached. The use of default assumptions has obvious dangers, however. In some cases it is precisely the haziness about intent which it is the function of the study to identify. It may well be prudent, therefore, at least to draw attention to the fact that such a default has been used.

30.39.6 Information acquisition and CAD interface

A large amount of generic information on physical, chemical and thermodynamic properties and on materials of construction is, in principle, available in standard databases. Data on the plant itself are available in the design databases. The information acquisition problem relates to that part of the information required which is not available from these sources.

Information may be provided for use by a computer aid by manual input, by retrieval from the system's own database or by accessing the database of another system. Manual input imposes an overhead which can make the use of the aid much less attractive. There is therefore a strong incentive to obtain the information required automatically.

One approach to information acquisition is to provide a database which is intended to meet in full the information needs. Another is to rely completely on the interactive provision of data by the user. An intermediate, or hybrid, approach is to provide the database with a substantial amount of information but to anticipate some user input of data.

As indicated, a method of identifying the items of information needed to solve a particular problem but still missing in the database is to perform a dummy run for the sole purpose of such identification.

Use may also be made of heuristics. One strategy for automatic acquisition is to exploit the implications of the plant configuration. One example is that the presence of a water separator implies free water in the feed to it and hence a hazard of generation of static electricity. Another is that the presence of a trip implies a hazard against which the trip is guarding. And so on.

The aim must be that the hazard identification tool acquires most of its information by accessing a CAD system and its associated databases. Here it is sufficient to note that facilities for interfacing such an aid to the CAD systems in general use are not yet universally available.

30.39.7 Plant configuration features

As mentioned earlier, a plant design may possess configurational features which point to potential hazards. Such undesirable features include those associated with (1) pressure relief, (2) shut-in pipework, (3) water hammer, (4) throttling of pump suction and (5) emergency isolation of hazardous inventories. As a simple example, where a plant configuration shows a long pipeline terminating in a shut-off valve, there is a presumption that water hammer might occur.

It is for consideration at what stage identification of such undesirable configurational features should be undertaken. One policy is to leave them to be identified in the course of the main hazard identification procedure. An alternative, and perhaps preferable, policy is to conduct a preliminary screening for such features.

30.39.8 Plant system decomposition

Success in the analysis of a plant system can often depend on the appropriateness of the decomposition. It is therefore worth devoting some effort to ensuring that the system is decomposed in the way best calculated to achieve the desired results.

In most methods decomposition is into units and lines, together with source and sink units representing the main inflows and outflows across the plant boundaries. Another element which it may be convenient to use is an offtake. This is any feature through which a flow can occur out of a line or unit and includes an atmospheric vent, a pressure relief valve, a drain or sample point, etc.

There is an issue as to whether a line between units should be handled as a whole or decomposed into its constituent parts, with each fitting such as a valve or filter treated separately. Similar choices apply to the units. A pump set or a valve and bypass set may each be treated as a single unit or decomposed further.

30.39.9 Model hierarchies and inheritance

It is becoming increasingly common to model the plant as a hierarchy of objects and to exploit the concept of inheritance. The head of the hierarchy may be taken as the plant itself. In this case the plant object contains the connectivities between the units, which are the next level of object.

The models of the units may also be ordered in hierarchies. Thus, for example, one model hierarchy may be headed by a pressure raiser, which is the parent for compressors, fans, pumps, etc. A given unit may belong to more than one hierarchy. Thus a centrifugal compressor may belong both to the hierarchy of pressure raisers and of rotating machines. Benefits of ordering the unit models in a hierarchy are that this provides structure in the model library and that models can inherit characteristics.

Inheritance is a valuable feature but needs to be applied with care, particularly where multiple inheritance is involved. Options in respect of inheritance from a parent unit are (1) to accept the whole set of characteristics, (2) to suppress the whole set of characteristics or (3) to accept the set of characteristics but to overwrite some of them. A declaration of the option exercised should be attached to the model.

For inheritance to be practised successfully it is necessary that the characteristics of the parent model be expressed in a way which is sufficiently general. As indicated earlier, one aspect of this is that the faults in the model need to be generic.

30.39.10 Units as objects

One way of generating faults is to list the attributes of a unit as an object. This provides a fault generator for the unit. This concept may be illustrated in terms of the properties of a pump. A pump:

(1) has problems –
loss of power; loss of lubrication; loss of cooling; cavitation; deadheading; reverse flow; vibration.
(2) causes problems –
can cause loss of flow; can cause loss of pressure; can cause power surge (start-up and shutdown); can cause vibration;
(3) is an equipment –
has states; has foundations; has connections; requires operation/control; requires maintenance;
(4) is an equipment which has states –
has operational state; has short-term stand-by state; has long-term stand-by state (mothballing);
has breakdown state; has maintenance state;
(5) is an equipment which requires operation/control –
requires to be started up; may require preliminary conditions/activities before start-up;
requires to be shut down; may require observable operation (visual, audible cues about start-up, running, etc.); may require remote operation; may require synchronized operation (e.g. with an emergency isolation valve);
(6) is an equipment which requires maintenance –
requires access; requires mechanical isolation; requires electrical isolation; may require lifting gear;
(7) is a machine –
(a) requires power; has motion; dissipates energy; has inertia;
(b) has rotary motion; has bearings; has seals;
(8) is a pressure raiser –
is a source of low pressure (inlet); is a source of high pressure (outlet);
(9) is a flow device –
causes turbulence; may have cavitation;
(10) has subsystems –
may have lube oil system; may have water cooling system;
(11) is a leak source –
has hazardous area classification;
(12) has reliability engineering requirements –
has reliability requirement; has availability requirement.

30.39.11 Faults and susceptibilities

Susceptibilities

Closely related to the foregoing is the concept of looking at a unit in terms of its susceptibilities. This also is perhaps best explained by way of example. Consider a water separator. Some rules for this might be:

(1) If the residence time is low, then the outflow liquid may contain free water.
(2) If the operator fails to drain the water, then the outflow liquid may contain free water.
(3) If interfacial effects occur (emulsion), then the outflow liquid may contain free water.
(4) If the liquid is one susceptible to charge generation (low conductivity) and the liquid velocity is high or there is a charge generator (e.g. filter) in the inlet line, then there is a hazard of static charging and discharge.

Similarly, for a heat exchanger:

(1) If the exchanger is new/recently cleaned, then the outflow process liquid temperature may be high.
(2) If the exchanger is old, then fouling may have occurred and the outflow process liquid temperature may be low.
(3) If there is a tube leak and the heating fluid pressure is greater than the process fluid pressure, then the outflow process liquid will have minor component increase consisting of heating fluid.
(4) If the residence time is high and the process fluid is susceptible to polymerization, then the liquid may polymerize in the exchanger.
(5) If the liquid contains minor components which promote fouling, then fouling may occur.
(6) If the liquid contains minor components which attack the existing fouling film, then the outlet process liquid may contain debris.

The richness of the fault representation depends in large part on the imaginativeness with which unit susceptibilities are identified.

Conditional faults

The susceptibilities just described constitute a form of fault with an attached condition. The attachment of conditions to faults is important because it either limits the number of faults generated or increases the proportion eliminated, depending on the stage at which the conditions are applied.

As a further example of a conditional fault, wet steam may be characterized as a fluid which is erosive, but with the attached condition that the velocity is high. The erosiveness of the steam is a generic property, but the velocity is a condition to be met in the specific application.

Faults with external effects

A hazard identification aid should cater not only for faults which propagate through the plant but also to some degree for those which have an impact outside it. Examples are liquid overflow from a storage tank and its implications for the bund around the tank or discharge from a relief and it effects.

30.39.12 Expert rules

As indicated, a unit may be provided with a set of expert rules for both the generation and evaluation, or resolution of faults. In some cases generation and resolution may occur within the same unit, in others use has to be made of fault propagation between units.

As an example of the latter, more complex case, consider a pump with the rule set

Hook	*Generation*	*Resolution*
Has lube oil system	Lube oil system failure may cause flow of lube oil as impurity into process fluid if failure creates a leak path and if the pressure of lube oil is greater than the pressure of process fluid	Response required if and only if lube oil impurity in process creates a significant problem

At this point a potential fault has been generated but not resolved. It is not known whether lube oil in the process fluid is an unacceptable impurity. Now consider the transport of the lube oil impurity into a water separator. Applying the water separator rule, or susceptibility, given earlier:

If interfacial effects occur (emulsion), then the outflow liquid may contain free water.

This rule effectively defines, for this unit, the nature of the potential problem. Whether or not the lube oil impurity is a significant problem depends on whether it is a foaming agent. This is determined from the fluid model, which is now described.

30.39.13 Fluid and stream models

Modelling of the units in terms of fault propagation and expert rules needs to be complemented by modelling of the fluid. A distinction is made between the fluids and the streams. 'Fluid' refers to the chemical substance, or mixture, which has generic properties. 'Stream' refers to the stream at a given location in the specific plant. A stream is defined primarily in terms of the fluid and of the pressure and temperature.

Some elements of the fluid and stream models are (1) stream definition, (2) stream transformations and (3) stream displacements.

Stream definition

A stream at equilibrium is defined basically in terms of its composition and of the pressure and temperature. The composition may be defined in terms of (1) bulk components, and (2) minor components, intended and unintended. The stream composition and the operating conditions of pressure and temperature define the phase and the physical properties of the equilibrium fluid.

Stream transformations

Much stream behaviour may be characterized in terms of transformations. These are (1) intended transformations and (2) unintended transformations. The intended transformations are what the process is all about, typically reaction and separation. The unintended transformations are what the exercise seeks to identify.

Stream interactions

Another way of categorizing stream behaviour is in terms of interactions. These are (1) interactions with operating conditions, (2) interactions with other materials and (3) interactions with other features.

Stream interactions with operating conditions

There are three categories of stream interaction with operating conditions: (1) phase, (2) flow properties and (3) reaction.

Phase transformations are (1) vaporization, (2) condensation, (3) melting and (4) solidification. These transformations may be partial or total.

Flow property transformations are any transformation which affects the flow properties of the fluid, e.g. viscosity change and change to slugging flow.

Reaction may occur within the fluid itself. This reaction may be in a reactor, where the reaction may be the intended reaction or also an unintended one; or it may be in another part of the plant, where it will almost always be an unintended reaction.

Stream interactions with other materials

There are a large number of stream interactions with other materials which may be conceived. The interactions considered here are confined to those which are due to the fluid constitution (composition and properties) and do not extend to the fluid motion.

The interactions include those with other materials such as (1) other fluids (bulk components, minor components), (2) catalyst, (3) materials of construction, or corrosion (main components, minor components), (4) air, (5) water, and (6) additives (interfacial agents, promoters, inhibitors). In each case it is necessary to consider the interaction both of the bulk components and of the minor components of the stream.

Interactions of the stream with the materials of construction include interactions of the stream both with the main components and with minor components such as gaskets, seals, trims, etc. Lubricants and sealing fluids may be treated as 'minor components'.

Air and water might be treated on a par with the other unintended minor components, but they are so common, and incidents associated with them so frequent, that they perhaps deserve special status. One aspect of this is that consideration should be given to whether or not they are declared as specific components of the stream.

Stream interactions with other features

Streams also interact with other features in the sense that a problem arises from the combination of the stream and the feature. These features include (1) units, (2) unit faults, (3) operations and (4) maintenance.

An example of an interaction between the stream and a unit is the case where the fluid is flammable and is transferred into a road tanker. There is a recognized hazard of static electricity in some cases.

An example of an interaction between the stream and a unit fault is the case where the stream contains gunk which causes blockage.

An example of an interaction between the stream and an operation is the case where a gravity separator is used to remove water from a toxic solvent with which it

is nearly (but not totally) immiscible and the water is drained off the bottom. The water will be saturated with the solvent and the latter will therefore exert its full vapour pressure. If the solvent is toxic, this may affect the operator.

An example of interaction between the stream and maintenance is the case where the fluid is very toxic and special precautions will need to be taken when the plant is broken open.

30.39.14 Fluid and stream models: hydraulics

A quite different set of fluid phenomena are those which fall into the broad category of hydraulic effects. One way of looking at these is in terms of the displacement of one fluid by another.

Displacement of gas by liquid

Displacements of gas by a liquid include (1) displacement in a vessel, (2) displacement in a pipe, (3) condensate hammer, (4) liquid lock and (5) siphon.

The pipe displacements are (1) permanent, flowing displacement (2) a moving liquid slug and (3) an essentially immobile liquid slug.

Displacement of gas by a liquid in a vessel can cause overflow and overpressure. Displacement of gas by a liquid in a pipe can cause erosion and incorrect measurement and control. Condensate hammer can cause damage to pipework and machinery. Liquid lock can prevent gas flow and pressure equalization.

Displacement of liquid by gas

Displacements of liquid by a gas include (1) displacement in a vessel (partial, total), (2) displacement in a pipe and (3) gas lock.

Displacement of liquid by a gas in a vessel can cause loss of head and overpressure. It can also take the form of gas breakthrough when a liquid seal at the bottom of a vessel is lost. Displacement of liquid by a gas in a pipe causes incorrect measurement and loss of control. Gas lock can prevent liquid flow.

Displacement of liquid by liquid

Displacement of liquid by a liquid occurs in rollover. Rollover is caused by the formation of two liquid layers and by inversion of the densities of the two layers.

30.39.15 Fluid and stream models: modelling strategy

A strategy for modelling the fluid needs to deal both with the identification and with the resolution of stream-related problems.

Stream problem identification

Stream-related problems arise from the three sorts of stream interactions and from stream hydraulics. One strategy for dealing with stream interactions is the use of breakpoints. A breakpoint is defined as a point in the plant at which the fluid constitution (composition and properties) and/or the operating conditions undergo or may undergo a significant change. This definition covers both a point where a change is intended and one where no change is intended but may nevertheless occur. It is for consideration what constitutes a significant change.

At each such point the three types of stream interaction are examined, to identify any problems. The default assumption is that unless there is information to the contrary, the stream passes through a breakpoint with its constitution and operating conditions unchanged except as given in the design.

Stream hydraulic problems tend to be related to particular types of line and unit. One way of dealing with these is therefore by using lines and units as the hooks for the appropriate expertise.

Stream problem resolution

Fault generation needs to be followed by fault resolution. The stream model should contain aids to assist in determining whether a generic fault identified by the fault generation process is in fact a significant problem in the specific case.

Some types of resolution aid include (1) landmark values, (2) susceptibility rules and (3) other rules. Here rules are taken to include related forms such as truth tables.

30.39.16 Fluid and stream models: information

The implementation of such a strategy requires the handling of information, which may be broken down into (1) information requirements, (2) information representation and (3) information acquisition.

The foregoing approach to the fluid and stream models implies the need for information on (1) inlet streams and (2) intended stream transformations at breakpoints, and information relating to the potential for (3) unintended stream transformations, (4) unintended stream interactions with other materials, (5) unintended stream interactions with other features and (6) unintended stream hydraulic effects.

The set of inlet fluids is those fluids entering at the boundaries and includes process fluids and utility fluids. The set of intended stream transformations is, in effect, the process.

The unintended stream transformations arise from the first two types of interaction (with the operating conditions and with the other materials). The unintended stream interactions with other materials may result in stream transformations, as just mentioned, and/or in other effects.

This part of the information relates to fault generation. The second part is that which relates to fault resolution. In large part this latter is concerned with various types of susceptibility to stream changes.

A large part of the fluid model consists of information about susceptibilities and incompatibilities. These relate to the three types of interaction already described, which are (1) stream–stream interaction, (2) stream–materials interaction, and (3) stream–feature interaction. These interactions occur essentially due to the fluid properties of the stream(s).

There are also interactions due to stream properties such as pressure and temperature. These include (1) pressure–materials interaction and (2) temperature–materials interaction.

Information on susceptibilities and incompatibilities is most naturally represented as rules or look-up tables.

30.39.17 Materials of construction model

Another model required is the materials of construction model. What this model should provide is the susceptibilities of the materials in the plant to undesirable interactions. The most elementary form of model is one which gives the incompatibilities between the materials of construction of the main items of equipment and the fluids. More useful is a model which also gives this information for (1) minor components of the main plant items and (2) for impurities in the fluids.

The materials model should also cater for susceptibilities of the materials to the stream properties of pressure and temperature. The materials model may be extended to give some information on effects. In most cases the basic effect is corrosion. The significance of this, however, varies. It may lie in its potential to cause a leak or in contamination of the fluid.

30.39.18 Filtering of faults

The output given by current computer aids for hazard identification tends to be too indiscriminate and too voluminous. As pointed out in Chapter 8, in a conventional hazop the identification of hazards is only one part of the activity; the other part is the filtering out of those hazards which are unfeasible or negligible.

Four forms of filtering can be distinguished: (1) suppression, (2) consolidation, (3) evaluation and (4) masking. These are now considered in turn.

Suppression of faults

By 'suppression' is meant suppression of the consequences and/or causes during the generation process or immediately thereafter. It has its place, but carries with it certain dangers. Suppression needs to be governed by suitable rules, which may not be easy to devise.

An example of suppression which may well be appropriate is the suppression of generalized blockage and leakage faults which tend to proliferate in certain aids, particularly where each fitting in a line is the subject of a separate examination.

Consolidation of faults

Consolidation of faults involves replacing a set of faults by a more limited set of equivalent faults. It is applicable mainly where a line has been decomposed into its constituent elements, each with its associated fault set. The use of consolidation requires suitable rules, the formulation of which may not be trivial. This contrasts with suppression, which is readily implemented.

Evaluation of faults

Evaluation of faults may take several forms. One is the application of expert rules, another is the use of landmark values and a third is the use of susceptibility data. Some types of rule for evaluation include those associated with (1) consequences, (2) product of consequence and frequency, (3) frequency, (4) classic hazard situations, (5) plant equipments, (6) protective devices, (7) unrevealed failures and (8) process variables.

There will be some events so serious that they are unacceptable virtually regardless of the frequency. There will be others where the product of consequences $\times$ frequency is an appropriate filtering criterion. There may be others, applicable to low consequence events, where only the frequency is of interest. There are certain classic situations such as thermal expansion of blocked-in fluid. There are certain pieces of equipment such as pump sets where there are classic hazards and solutions. There are certain classic aspects of protective devices such as a pressure relief valve where the set pressure may not be exceeded but where capacity may be. There are certain rules, displayed in hazops, as to how to handle unrevealed failures, particularly in instruments. There may be rules governing process variables such as level or pressure. One way of developing evaluation rules is to identify the features which trigger interest on the part of members of a hazop team.

Another method of evaluation is the use of landmark values. These are most likely to be associated with the fluid model. A typical application of a landmark value is to determine whether the fluid is likely to undergo a change of phase such as boiling or freezing.

The third evaluation method mentioned above is the use of data on susceptibility or compatibility. This method is likely to be applicable mainly to the fluid and materials of construction models. Data on susceptibility may take the form of look-up tables or rules.

The account of evaluation which has just been given implies that the way to proceed is to generate all possible faults and then to evaluate each one to determine whether it can be rejected. There is an alternative approach to evaluation which is to reverse the 'burden of proof' and to apply the default rule that no fault is retained unless there is good reason to do so. This is possibly closer to the *modus operandi* of a hazop team. Whichever approach is adopted, the information and rules required to support the identification decisions are broadly similar.

30.39.19 Masking of faults

Whatever the extent and effectiveness of the various forms of filtering, there remains the question of whether to display in the output all the faults not removed by the filtering processes described or whether to practice some form of masking.

In principle, masking is a relatively simple operation. It involves defining within the total information a subset which is not to be displayed and laying a mask over it. There may be a number of masks, each with its subset, and they may overlap, like Venn diagrams.

A hierarchy of masks can be envisaged, with distinctions based on the severity of the failures involved, with a stringent mask for coarse hazard studies, etc. Alternatively the distinction may be based on the discipline involved, e.g. control systems, pressure relief systems, etc., for use by different parties to the design. There is also the option of user-configured masks.

30.39.20 Query and action outputs

The output from a conventional hazop study includes a list which is typically a mixture of queries and actions. The actions may vary in status from requirements to suggestions.

The corresponding output for a computer aid is likely to contain a different mix, weighted more to queries, with proposals for positive action probably confined to certain limited areas. Effort is better employed in improving the quality of the queries rather than in extending the aid into a design tool.

Table 30.16 *Some computer codes for fault tree synthesis*

Code[a]	*Methodology*	*Reference*
DRAFT	Failure transfer functions	Fussell (1973)
FTS	Digraphs	Powers and Tompkins (1974a,b); Powers and Lapp (1976); Lapp and Powers (1977a, 1979); Cummings, Lapp and Powers (1983)
CAT	Decision tables	Salem, Apostolakis and Okrent (1977); Apostolakis, Salem and Wu (1978); Salem and Apostolakis (1980)
-	Digraphs	D.J. Allen and Rao (1980); D.J. Allen (1984)
CAFTS	Transfer logic models, mini-fault trees	Poucet and de Meester (1981); Poucet (1983, 1990)
RIKKE	Equation 'bigraphs', transition tables	J.R. Taylor (1982)
FAULTFINDER	Propagation equations, mini-fault trees	Martin-Solis, Andow and Lees (1982); B.E. Kelly and Lees (1986a–e); Mullhi *et al.* (1988); A. Hunt *et al.* (1993a-e)
AFTC	Decision tables	Sang Hoon Han *et al.* (1989)
FTSA	Causal trees, transition tables	Bossche (1991a-c)

[a] Synthesis codes usually have a drafting package also.

30.39.21 Explanation facility

As described earlier, a standard feature of an expert system is the explanation facility. There is, in principle, no reason why such as facility should not be provided as part of a hazard identification aid, to be consulted in the probably small number of cases where the logic of the argument is unclear to the user.

30.40 Fault Tree Analysis

A large number of computer programs have been developed for the analysis of fault trees, which are often very large. The tasks carried out by these programs fall mainly into four categories. These are determination of:

(1) minimum cut sets;
(2) common cause failures;
(3) reliability and availability;
(4) uncertainty.

Some of these codes are listed in Table 29.7. This table gives the references to the codes listed. Further references are given in Table 29.1. One of the first sets of codes was PREP and KITT developed by Vesely and co-workers. PREP obtains the minimum cut sets and KITT evaluates reliability and availability. There are two versions, KITT-1 and KITT-2, the latter having the capability of handling time-dependent failure data. These codes have been widely used and were utilized in the Rasmussen Report.

Another group of codes are those developed by Fussell and co-workers. These include MOCUS, BACFIRE and SUPERPOCUS for determining minimum cut sets, common cause failures and reliability and availability.

Codes for the determination of importance include IMPORTANCE, developed by Lambert.

The Rasmussen Report included several codes. SAMPLE combines input distributions to give an output distribution. MOCARS determines the distribution of a tree top event.

30.41 Fault Tree Synthesis

As just described, there are available a number of computer codes for the analysis of fault trees. The synthesis of fault trees is a more difficult problem, but some progress has been made in developing aids for this. Again the codes utilize some form of fault propagation modelling.

30.41.1 Fault tree drafting

Some codes for fault tree construction are aids to the manual synthesis of fault trees. They include TREDRA and TREE.

30.41.2 Fault tree synthesis codes

There are a number of codes which have been developed to effect the automatic synthesis of fault trees. The different methods take different starting points, including: functional equations (e.g. B.E. Kelly and Lees, 1986a); graphical methods such as digraphs (e.g. Andrews and Morgan, 1986); reliability block diagrams (e.g. Caceres and Henley, 1976) and reliability graphs (e.g. Camarda, Corsi and Trentadue, 1978); logic models (e.g. Poucet, 1983) and logic flowgraphs (e.g. Guarro and Okrent, 1984); tabular methods, such as decision tables (e.g. Salem, Apostolakis and Okrent, 1977) and transition tables (e.g. J.R. Taylor, 1982; Bossche (1991a–c); and mini-fault trees (e.g. Fussell, 1973a,b; B.E. Kelly and Lees, 1986a).

Some of these codes are summarized in Table 30.16. Most are probably best characterized as research codes. An account is now given of some of these methods.

30.41.3 DRAFT

An early code for fault tree synthesis was the DRAFT code of Fussell (1973a,b). He used models which he termed component failure transfer functions, which are effectively a form of mini fault tree. He applied his method, which he called the Synthetic Tree Model, to electrical systems rather than process plants, although

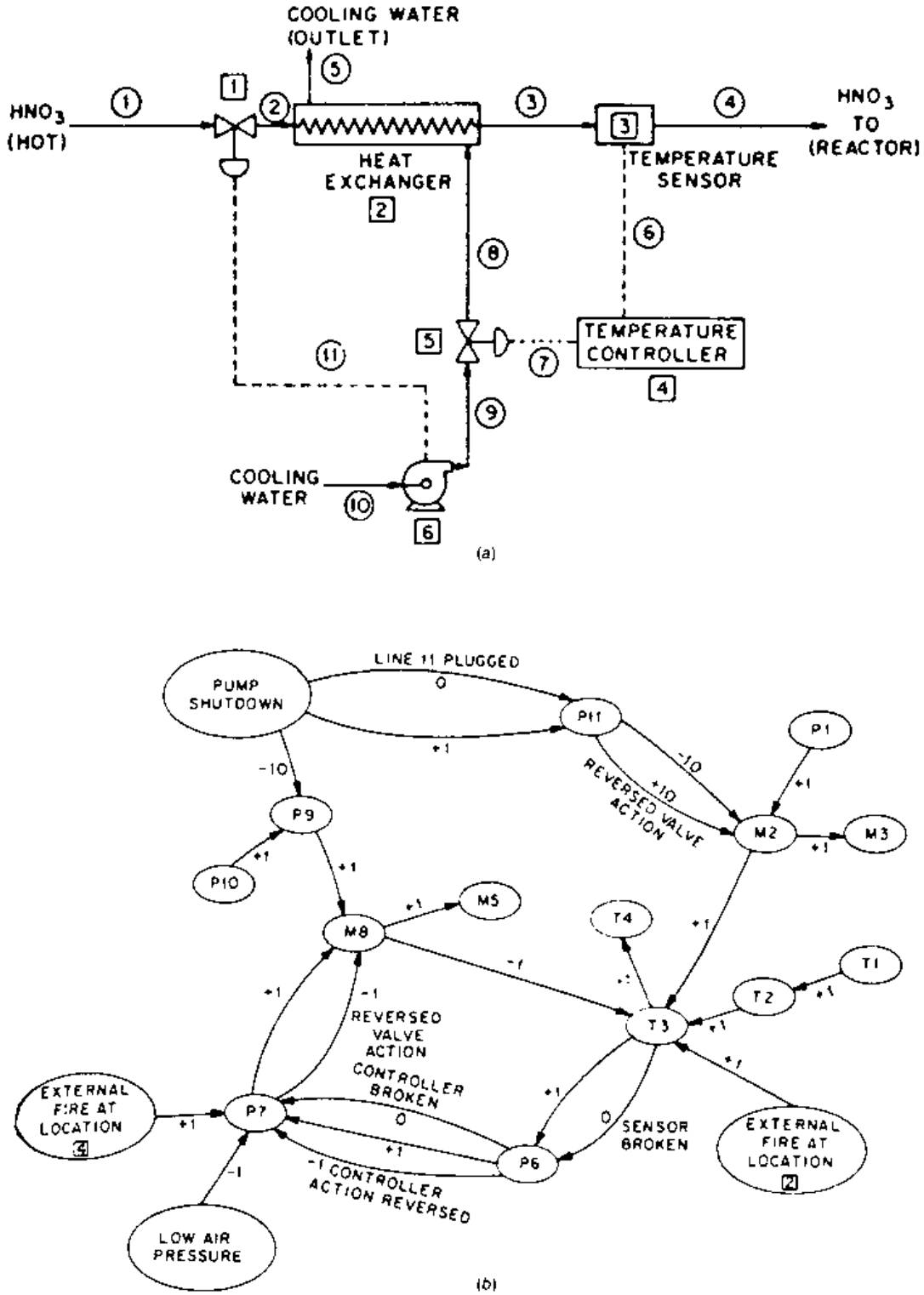


Figure 30.17 *A nitric acid cooler system (Lapp and Powers, 1977a): (a) flow diagram; (b) digraph (Courtesy of the Institute of Electrical and Electronic Engineers)*

the electrical systems considered were on process plant systems.

30.41.4 FTS

The first fault tree synthesis code for process plants was the FTS code of Powers and Tompkins (1974a,b), further developed by Powers and Lapp (Powers and Lapp, 1976; Lapp and Powers, 1977a,b). These authors model the plant system using digraphs. Figure 30.17(a) shows the nitric acid cooler system used by Lapp and Powers, which has become a classic example, and Figure 30.17(b) shows the digraph given by the authors for this system.

The fault tree is constructed by selecting the node for the top event of interest and then developing the tree for the causes of this event. For a given node, the causes are the inputs to the node. The tree is developed down to the basic events. Causes which violate consistency are deleted.

Control loops are handled by means of an operator, which is essentially a loop structure imposed at the appropriate point in the development of the tree. Separate operators are used for feedback and feedforward loops.

The fault tree obtained in this work has been subject to some discussion in the literature (e.g. Lambert, 1979; Lapp and Powers, 1979; Locks, 1979; Yellman, 1979).

30.41.5 CAT

Another early code for the synthesis of fault trees for process plants was the CAT code of Salem, Apostolakis and co-workers (Salem, Apostolakis and Okrent, 1975a,b, 1977; Apostolakis, Salem and Wu, 1978; Salem and Apostolakis, 1980). In the CAT code the models used are cast in decision table form. The tree is then constructed by nominating a top event and developing its causes by selecting from the appropriate entries of the decision tables, using suitable procedures to maintain consistency.

30.41.6 RIKKE

The RIKKE code of J.R. Taylor (1982) utilizes so-called equation 'bigraph', transition table and mini-fault tree models. The construction of the tree proceeds by selecting a top event and developing its causes by tracing through the mini-fault trees, with procedures to maintain consistency. Taylor characterizes his fault construction algorithm as utilizing a component-by-component construction and contrasts it with that of Lapp and Powers, which he describes as a loop-by-loop method. A feature of Taylor's method is the use of a larger set of deviations than simple HI and LO, such as VHI and DIST HI.

30.41.7 FAULTFINDER

Another code for fault tree synthesis is the FAULTFINDER code of B.E. Kelly and Lees (1986a–e) and A. Hunt *et al.* (1993a–e). This is described in the following section.

30.41.8 Loop structure methods

The methodology for fault tree construction described is essentially component oriented, but this is not the only approach which may be adopted. An alternative is a structure oriented method in which the structure of the tree is determined from the outset by that of features such as the control and trip loops. This type of approach is illustrated in the work of Shafaghi, Andow and Lees (1984) and Shafaghi, Lees and Andow (1984).

30.42 Fault Tree Synthesis: FAULTFINDER

A more detailed account is now given of one particular code for fault tree synthesis. This is the FAULTFINDER code described by B.E. Kelly and Lees (1986a–e) and A. Hunt *et al.* (1993a–e).

In this work the models are formulated initially in terms of functional equations of the type described in Section 30.36. The building blocks for the fault tree synthesis, however, are mini-fault trees, described in the earlier work of Martin-Solis, Andow and Lees (1982). The mini-fault trees are constructed automatically from functional equation models.

The overview of FAULTFINDER which follows, both illustrates another application of fault propagation modelling and serves as an example of a fault tree synthesis code. The description is necessarily highly simplified.

30.42.1 System decomposition

The system decomposition is essentially similar to that used in the HAZID code. The piping and instrument diagram is converted to a block diagram and for each unit in the latter a unit model is specified, drawing on a library of models, with additional models configured by the user if necessary.

It is also necessary to provide certain structural information. The main information required relates to the control and trip loops. For each loop the instruments comprising the loop and the streams immediately affected by the action of the loop are identified.

30.42.2 Unit and top event models

The code uses the basic fault propagation methodology described in Section 30.36. A plant unit is modelled in the first instance using any combination of three forms: propagation equations, event statements and decision tables. The propagation equations are used to represent the propagation of a disturbance, or fault, through a unit and the event statement to describe the initiation of a fault in a unit. The decision tables are used mainly to represent relations involving AND gates.

From these three forms of input are constructed the mini-fault trees for the units. For each output from the unit there are at least two mini-trees, one for the deviation HI and one for LO. The top event of a mini-tree, therefore, is a deviation of an unit output. The mini-tree has only one level below this top event, the events in this level consisting of either variable deviations or basic faults.

The derivation of a mini-tree in a unit model proceeds as follows. Consider the relation given earlier for flow through a pipe

$$Q_2 \text{ out} = f(G_1 \text{ in}, G_2 \text{ out}) \qquad [30.42.1]$$

and the event statements

$$\text{PART-BLK: } Q_2\text{out LO} \qquad [30.42.2]$$

$$\text{LK-LP-EN: } Q_2\text{out LO} \qquad [30.42.3]$$

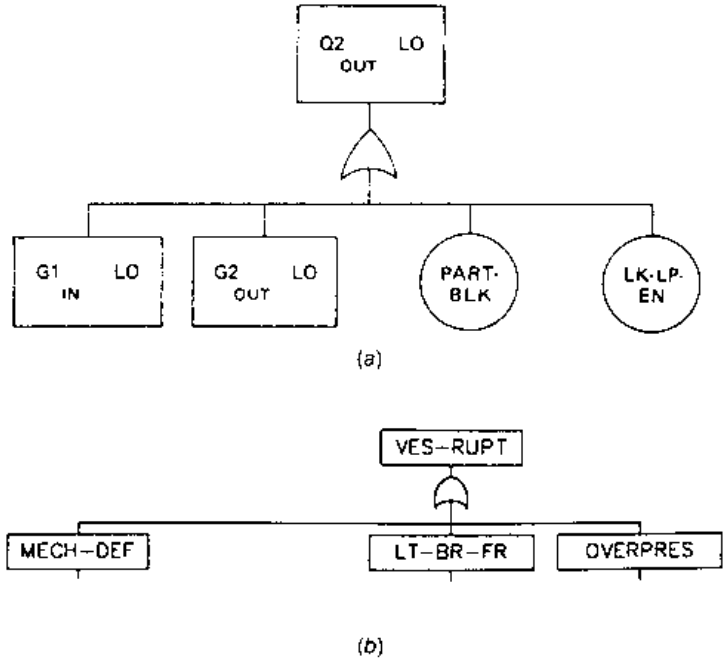


Figure 30.18 *FAULTFINDER: some mini-fault trees (after B.E. Kelly and Lees, 1986a; A. Hunt et al., 1993e): (a) mini-fault tree for event Q_2 LO (LK-LP-EN, leak to low pressure environment; PART-BLK, partial blockage); (b) mini-fault tree for top event VES-RPT (vessel rupture) (LT-BR-FR, low temperature brittle fracture; MECH-DEF, mechanical defect; OVERPRES, overpressure)*

The propagation equation states that Q_2 is LO if G_1 or G_2 is low. The event statements state that Q_2 is LO if there occurs the fault PART-BLK (partial blockage) or the fault LK-LP-EN (leak to low pressure environment). The resultant mini-tree is shown in Figure 30.18(a). Separate but very simple mini-tree models are used for the top events. Figure 30.18(b) shows a top event model for the event VES-RPT (vessel rupture).

The configuration of a unit model is carried out using the model generation program. The data are entered on a proforma essentially similar to that used in HAZID and shown in Figure 30.15, but the output generated by the program consists in this case of the set of mini-fault trees for the unit.

The methodology includes various aids to reduce the modelling effort, and to achieve a degree of automatic modelling. There is a facility to generate automatically the event statements for certain standard faults at ports. There are programs and template models for the configuration of vessels. And there are also some basic archetypes of other units such as reactors and heat exchangers.

30.42.3 Fault tree construction

Fault tree construction starts by nominating a top event, retrieving first the appropriate top event model and then the unit mini-trees which have as their top event the causes of the variable deviations which are the causes of the top event. The causes of the top events in this first set of mini-trees are then in turn developed using further mini-trees. The development continues until the base events in the mini-trees are either basic failures or events crossing the boundaries of the system. The principle of tree construction is therefore very simple. The complications arise mainly in ensuring consistency and in handling certain structures in the plant.

30.42.4 Tree consistency

There are two main types of consistency which need to be maintained: series consistency and parallel consistency. In essence, series consistency means that an event cannot be caused by its obverse. Also it cannot be caused by itself. An event may also be inconsistent with certain faults. Series consistency is checked as the tree is developed. Parallel consistency is the consistency of events in one branch of the tree with events in other branches of the tree under an AND gate. The check on parallel consistency is made during the rationalization stage which follows construction of the crude tree.

30.42.5 Tree structures

It is found that there are certain structures in a plant which need to be given special treatment, notably control loops, trip loops and divider-header combinations. The fault tree for a plant may be regarded as a composed of a basic demand tree, devoid of all control and trip loops,

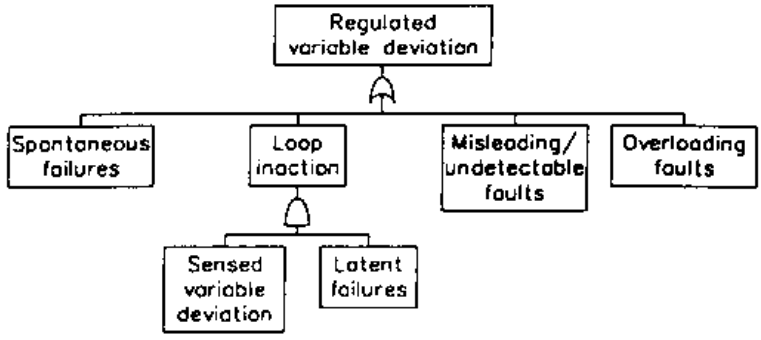


Figure 30.19 *FAULTFINDER: template for a controlled variable deviation, in either a feedback or a feedforward loop (A. Hunt et al., 1993c) (Courtesy of Elsevier Science Publishers)*

with the control and trip branches then added to it. Manual construction of a fault tree essentially proceeds by creating first the demand tree and then adding the control and trip branches. The structure of the tree is largely determined by these features.

It is desirable that an automatically constructed tree retain this general structure. But in any case it is found that problems arise in the construction of the tree unless some information on the control and trip loop structure is explicitly provided. It is possible in principle to limit the input information to the basic unit connectivities and to have the program identify the loops, but it is simpler to provide this information as part of the input.

Another type of structure which needs special treatment is combinations of dividers and headers. These occur in many guises, such as the suction and delivery manifolds of a pair of pumps or a control valve with a bypass. In some cases divider–header combinations are nested and in others they are staggered. In the case of divider–header combinations manual identification is complicated, and the program is provided with an algorithm to effect identification.

For the control and trip loops, use is made of templates which impose a structure on the tree at the point in tree development where the loop is encountered. For control loops use is made of three such templates. One of the templates, shown in Figure 30.19, is for a controlled variable in either a feedback or feedforward loop. The other two are for a manipulated variable, one in a feedback loop and the other in feedforward loop.

For trip loops a distinction is made between functional failure (failure to operate on demand) and operational failure (spurious trip). A template is used for functional failure, but not for operational failure, which is treated on a par with any other failure which disturbs the system.

30.42.6 Fluid and materials of construction models

The methodology allows for the supplementation of the unit models by models for the process fluids and for the materials of construction. Essentially, these models handle various kinds of susceptibility, whether to phase change or to corrosion. The general approach is similar to that used in the HAZID code.

30.42.7 Tree rationalization

Once the crude fault tree has been constructed it is necessary to rationalize it. Rationalization involves a number of operations., These include: checking for parallel consistency; elimination of certain branches where the base event is impossible or, alternatively, certain; and rationalization of the branches of control loops. It is at this stage that the attachment of the trip loop functional failure branches occurs, the treatment during the initial construction being limited to identification of the variables which are protected by the loop.

30.42.8 Sequential operations

A sequence of operations may be handled by treating each step separately and re-initializing the configuration at each step. An overall fault tree then takes the form of tree with a top event SEQUENCE FAILS, with the two events ANDed together at the next level down SEQUENCE FAILS AT STEP 1 and SEQUENCE FAILS AFTER STEP 1, and so on.

In this connection, it merits mention that the top event of a fault tree does not need to be a hazardous event. It can also be an event such as SEQUENCE ABORTS in, say, a computer controlled sequence.

30.42.9 Other features

The methodology also accommodates a number of other features. Changes to control and trip loop set points normally receive no special treatment. Control exercised by a human operator or process computer which is equivalent to a conventional control loop is modelled as a notional loop.

Failures of utilities may be modelled either as independent failures in individual units or as inputs from a common supply which is itself subject to complete failure. This latter method may also be used to model other common cause failures.

30.42.10 Model generation and model library

The general approach to model generation and to the model library in FAULTFINDER is that outlined in Section 30.36 for fault propagation in general and in Section 30.38 for HAZID. Unit models are stored in the

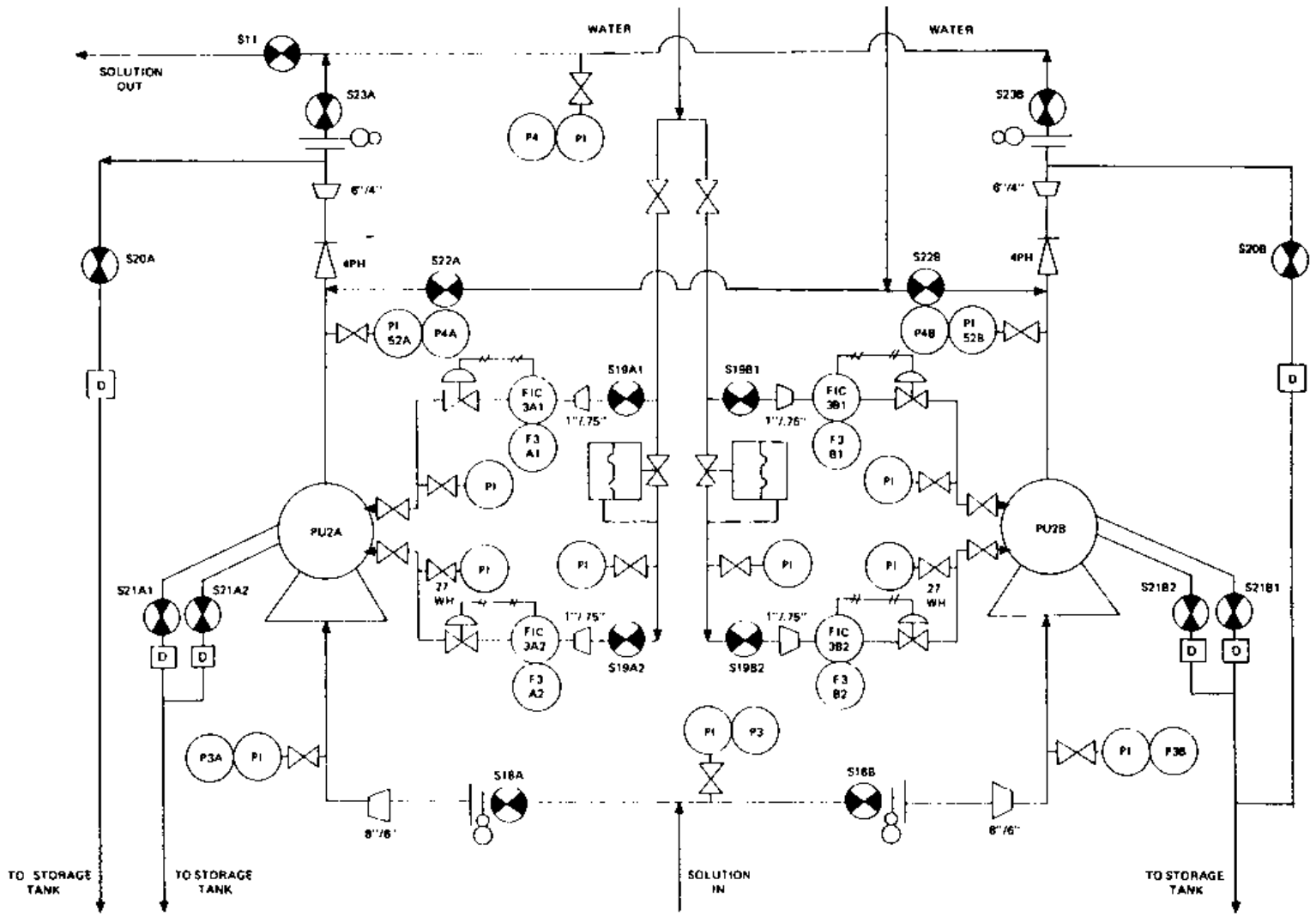


Figure 30.20 *FAULTFINDER: illustrative example – a pump system (B.E. Kelly and Lees, 1986d) (Courtesy of Elsevier Science Publishers)*

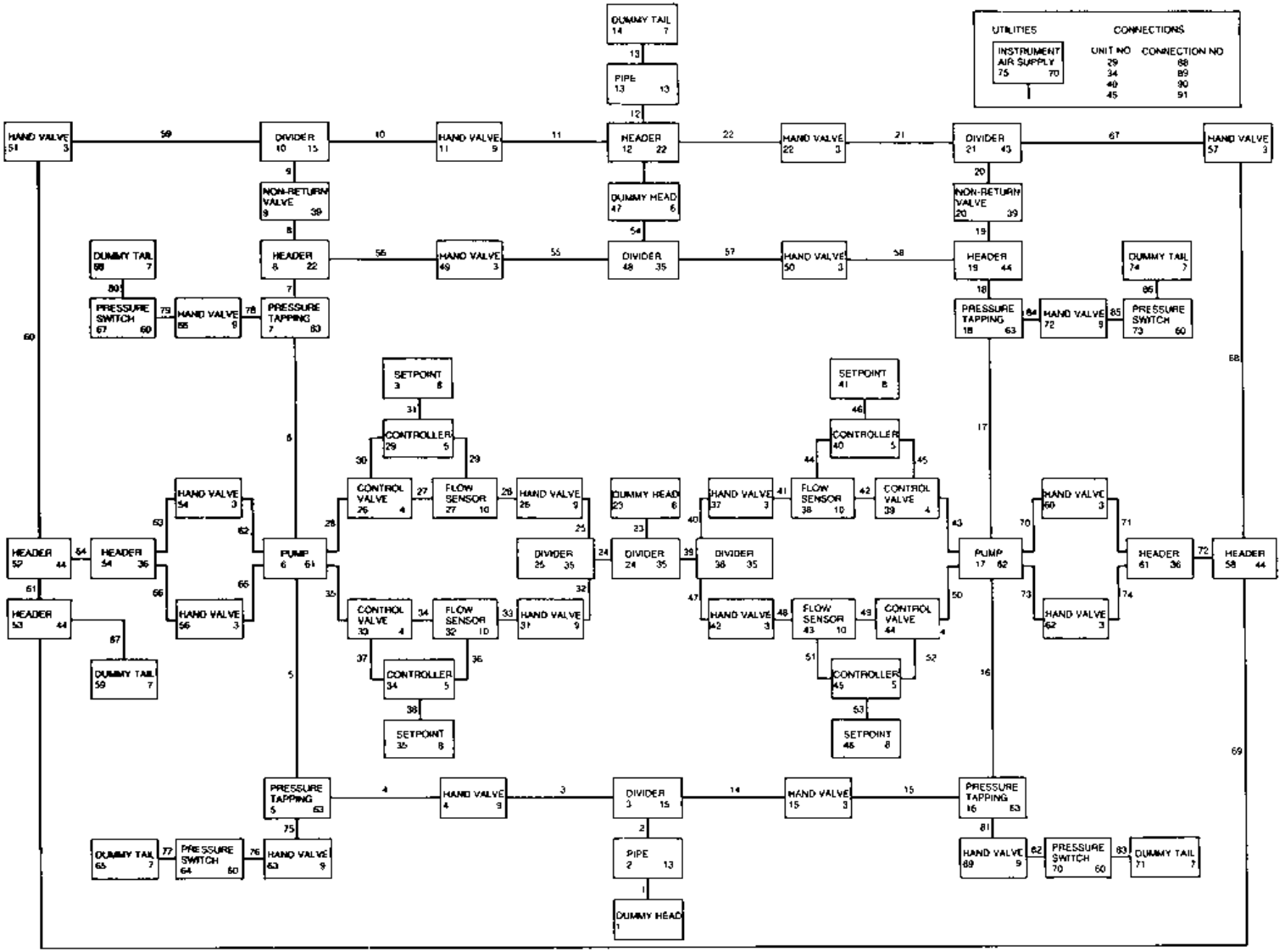


Figure 30.21 *FAULTFINDER: illustrative example – configuration block diagram for pump changeover system (B.E. Kelly and Lees, 1986d) (Courtesy of Elsevier Science Publishers)*

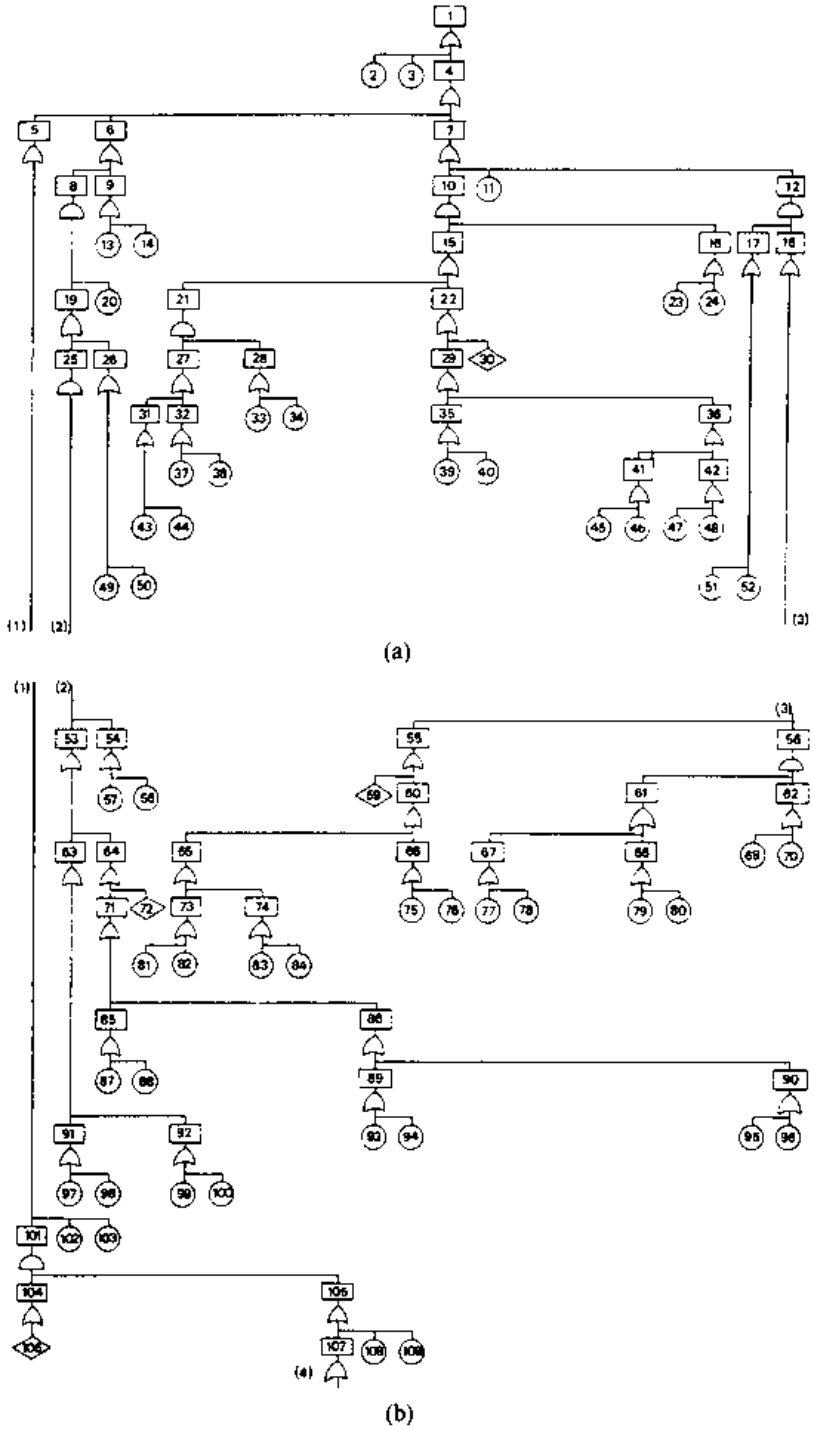


Figure 30.22 *FAULTFINDER: illustrative example – pump changeover sequence; fault tree for Step 8 (B.E. Kelly and Lees, 1986d) (see Table 30.17 for key) (Courtesy of Elsevier Science Publishers)*

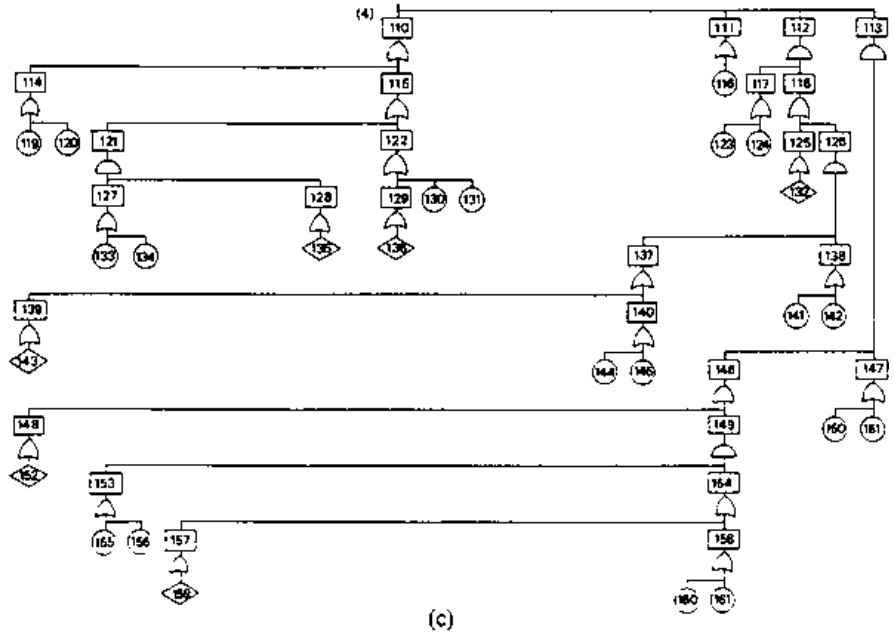


Figure 30.22 *continued*

unit model library as sets of mini-fault trees. Details of the library are given by B.E. Kelly and Lees (1986c) and A. Hunt *et al.* (1993a).

A new model is generated by completing a proforma on which are entered the functional equations, event statements and decision tables, if any, for the unit. The mini-fault trees of the model are then generated automatically. Generation of new models for vessels is assisted by the provision of a taxonomy of ports, by partial automation of the modelling of ports and by the use of a special vessel model generation program and of vessel archetypes, or templates.

30.42.11 Computer codes

The main programs in the FAULTFINDER package are: MASTER, which does the housekeeping; FAULT, which constructs the tree; and MODGEN and EVTGEN, which generate the unit models and top event models, respectively. There are model libraries for unit models and top event models. Use is also made of various other programs for fault tree drawing and of standard programs for fault tree analysis.

30.42.12 Illustrative example: pump changeover

Numbers of examples of fault trees constructed by the program are given in the accounts by B.E. Kelly and Lees (1986a–d) and A. Hunt *et al.* (1992a–e). A vaporizer example is given by Mullhi *et al.* (1988).

An illustrative example of fault tree construction using FAULTFINDER is given by B.E. Kelly and Lees (1986d). The system considered is the pump system shown in Figure 30.20. The problem was to identify the potential causes of abortion of a 14-step changeover sequence. The configuration block diagram is shown in Figure 30.21. The fault tree for Step 8 of the changeover is illustrated in Figure 30.22, the key for which is given in Table 30.17. The initial entries in the table of the minimum cut sets for this step, obtained by a fault tree analysis code, are shown in Table 30.18. The original paper gives further details, including listings of the steps in the sequence, the unit models used, the sequence steps and abort conditions, the configuration at each re-initialization and the minimum cut sets.

30.43 Operating Procedure Synthesis

There are relatively few computer aids for the examination of plant operations such as start-up and shut-down, although it is often in these phases that incidents occur, but progress is now apparent in the synthesis of operating procedures through the application of AI planning techniques. Pioneering work in this area was the study of Rivas and Rudd (1974) on the synthesis of operating sequences for valves.

With the progress made in AI planning techniques, operating procedure synthesis (OPS) for process plants has become a more active area. Studies include those done on valve operations by O'Shima (1983), on operating procedures by Fusillo and Powers (1987, 1988b) and Aelion and Powers (1991), on valve operations by Foulkes *et al.* (1988), on purging procedures by Fusillo and Powers (1988a), on operating procedures by Lakshmanan and Stephanopoulos (1988a,b, 1990) and Soutter and Chung (1995a,b) and on batch processes

Table 30.17 *FAULTFINDER: illustrative example – pump changeover sequence; key to fault tree for Step 8 (B.E. Kelly and Lees, 1986d) (Courtesy of Elsevier Science Publishers)*

No. in fault tree	*Text*	*No. in fault tree*	*Text*	*No. in fault tree*	*Text*
1	SEQ-F-AT Step 8	55	R61 REV	109	HV-F-SH Unit 15
2	SEN-F-HI Unit 67	56	P60 SOME	110	DT Row 1 Unit 17
3	SEN-F-STK Unit 67	57	HF-D-OP Unit 51	111	DT Row 5 Unit 17
4	P79 SOME	58	HV-F-OP Unit 51	112	R70 REV
5	DT Row 1 Unit 7	59	R87 REV	113	R73 REV
6	R7 REV	60	P69 SOME	114	P50 SOME
7	P6 SOME	61	P59 SOME	115	DT Row 1 Unit 19
8	R8 REV	62	A(DUMMY) Unit 52	116	SHUTDOWN Unit 17
9	P56 SOME	63	P64 SOME	117	A(DUMMY) Unit 60
10	R65 REV	64	R61 REV	118	R71 REV
11	STARTUP Unit 6	65	P72 SOME	119	HV-D-OP Unit 50
12	R62 REV	66	P68 SOME	120	HV-F-OP Unit 50
13	HV-D-OP Unit 49	67	R10 REV	121	R67 REV
14	HV-F-OP Unit 49	68	P9 SOME	122	DT Row 3 Unit 21
15	R66 REV	69	HV-F-OP Unit 51	123	HV-F-OP Unit 60
16	A(DUMMY) Unit 56	70	HV-D-OP Unit 51	124	HV-D-OP Unit 60
17	A(DUMMY) Unit 54	71	P69 SOME	125	R69 REV
18	R63 REV	72	R87 REV	126	P68 SOME
19	R9 REV	73	P71 SOME	127	A(DUMMY) Unit 57
20	NRV-F-OP Unit 3	74	P74 SOME	128	R68 REV
21	P60 SOME	75	HV-D-OP Unit 57	129	R22 NONE
22	R61 REV	76	HV-F-OP Unit 57	130	HV-D-SH Unit 22
23	HV-F-OP Unit 56	77	HV-D-OP Unit 11	131	HV-F-SH Unit 22
24	HV-D-OP Unit 56	78	HV-F-OP Unit 11	132	R87 REV
25	R59 REV	79	HV-D-OP Unit 49	133	HV-D-OP Unit 57
26	R10 REV	80	HV-F-OP Unit 49	134	HV-F-OP Unit 57
27	P59 SOME	81	HV-F-OP Unit 60	135	R87 REV
28	A(DUMMY) Unit 51	82	HV-D-OP Unit 60	136	R13 NONE
29	P69 SOME	83	HV-F-OP Unit 62	137	P67 SOME
30	R87 REV	84	HV-D-OP Unit 62	138	A(DUMMY) Unit 57
31	R10 REV	85	P68 SOME	139	R21 REV
32	P9 SOME	86	P72 SOME	140	P20 SOME
33	HV-D-OP Unit 51	87	HV-D-OP Unit 57	141	HV-F-OP Unit 57
34	HV-F-OP Unit 51	88	HV-F-OP Unit 57	142	HV-D-OP Unit 57
35	P68 SOME	89	P71 SOME	143	R13 REV
36	P72 SOME	90	P74 SOME	144	HV-F-OP Unit 50
37	HV-D-OP Unit 19	91	P63 SOME	145	HV-D-OP Unit 50
38	HV-F-OP Unit 19	92	P66 SOME	146	R74 REV
39	HV-D-OP Unit 57	93	HV-D-OP Unit 60	147	A(DUMMY) Unit 62
40	HV-F-OP Unit 57	94	HV-F-OP Unit 60	148	R69 REV
41	P74 SOME	95	HV-F-OP Unit 62	149	P68 SOME
42	P71 SOME	96	HV-D-OP Unit 62	150	HV-F-OP Unit 62
43	HV-D-OP Unit 11	97	HV-D-OP Unit 51	151	HV-D-OP Unit 62
44	HV-F-OP Unit 11	98	HV-F-OP Unit 51	152	R87 REV
45	HV-F-OP Unit 62	99	HV-D-OP Unit 56	153	A(DUMMY) Unit 57
46	HV-D-OP Unit 62	100	HV-F-OP Unit 56	154	P67 SOME
47	HV-F-OP Unit 60	101	P3 NOR	155	HV-D-OP Unit 57
48	HV-D-OP Unit 60	102	HV-D-SH Unit 1	156	HV-F-OP Unit 57
49	HV-D-OP Unit 11	103	HV-F-SH Unit 1	157	R21 REV
50	HV-F-OP Unit 11	104	P2 NOR	158	P20 SOME
51	HV-F-OP Unit 51	105	R14 NONE	159	R13 REV
52	HV-D-OP Unit 51	106	P1 NOR	160	HV-F-OP Unit 50
53	R60 REV	107	R15 NONE	161	HV-D-OP Unit 50
54	A(DUMMY) Unit 51	108	HV-D-SH Unit 15		

using qualitative process theory by Rotstein, Lavie and Lewin (1992).

Several of these studies are now described. But first it is pertinent to make one or two points on the relationship of OPS to AI planning

30.43.1 Unsafe states

In the application of planning to process operations it is obviously necessary to pay particular attention to the avoidance of undesirable, and especially of unsafe, states. Insofar as much AI planning work has been concerned with robots operating in blocks world, the question of unsafe states has tended to be less urgent. Techniques for handling the unsafe state problem are not well developed in AI planning. In process operations, however, the avoidance of unsafe states is very much to the fore.

The avoidance of unsafe states is an essential require-

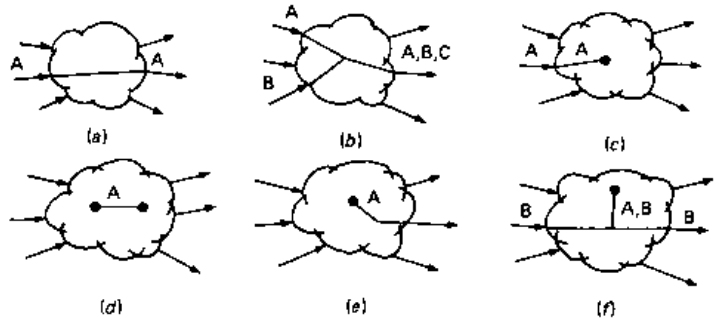


Figure 30.23 *Valve operations synthesis: states of chemical species (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Table 30.18 *FAULTFINDER: Illustrative example – pump changeover sequence; some minimum cut sets of the fault tree for Step 8 (B.E. Kelly and Lees, 1986d)*

Minimum cut set No.	*Cut set order*	*Unit No.*	*Faults*
1	1	4	HV-F-SH
2	1	6	STARTUP
3	1	49	HV-F-OP
4	1	67	SEN-STK
5	1	67	SEN-F-HI
6	2	9	NRV-F-OP
		11	HV-F-OP
7	2	54	HV-F-OP
		57	HV-F-OP

ment of an OPS planner and may well govern the choice of planning algorithm. In seeking to avoid unsafe states, an advantage lies with a planning strategy in which actions are added one at a time and the safety of the new state is confirmed before proceeding further; in other words with a forward-chaining, linear planner.

30.43.2 Valve operations

Much of the work described on OPS has been concerned with the synthesis of sequences of valve operations. From the point of view of planning, the crucial feature of valve operations is that they are not readily handled by a simple planning operator. The problem is that an action in which a valve is closed or opened does not have a unique set of effects. The effects depend on the state of the whole system. For example, if a line contains two valves in series, the effect of opening the upstream valve is not unique, but depends on whether or not the downstream valve is already open. One solution to the valve operations problem is to make use of domain specific knowledge.

30.43.3 Valve operations: method of Rivas, Rudd and Kelly

Historically, research in this area started with two pieces of work by Rudd and co-workers, one concerned with analysis and the other with the synthesis of valve operating sequences. Strictly, only the latter constitutes OPS, but it is convenient to describe first the work on analysis.

In their study, Rivas, Rudd and Kelly (1974) considered the analysis of a proposed valve sequence to determine whether it was hazardous. Such an analysis may be used to obtain a safe sequence for incorporation in operating instructions or it may be made the basis of a real-time software interlock system which leaves it to the operator to propose a valve sequence, but inhibits any hazardous sequence.

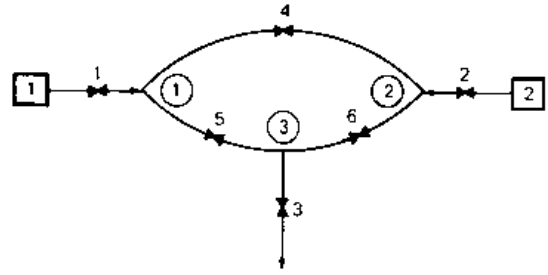


Figure 30.24 *Valve operations synthesis: network of connectors (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Figure 30.25 *Valve operations synthesis: nomenclature (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Table 30.19 *Design of valve sequencing operations: structure of a network of connectors (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Connector	*Node j*	*Node l*	*Connectors joined to node j*	*Connectors joined to node l*	*Species*	*Valves*
1	1		4,5	–	1	×
2	2		4,6	–	2	×
3	3		5,6	–		×
4	1	2	1,5	2,6		×
5	1	3	1,4	3,6		×
6	3	2	3,5	2,4		×

Table 30.20 *Design of valve sequencing operations: proposed valve sequence for a network of connectors (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Order of operation procedure	*Open valves*	*Closed valves*
1	1, 3, 5, 6	
2	2	1, 5
3	4	2, 3

The possible states of the chemical species are shown in Figure 30.23. In pattern (a) the species A flows through the system without other contact; in (b) species A and B join and share a common path through the system; in (c) A is stopped in the system by a closed valve; in (d) A is trapped within the system by two closed valves; in (e) A is eventually flushed from the system leaving the connector empty; in (f) A is held in the system not by closed valves as in (d) but by the driving force causing the flow of species B.

A simple network of connectors is shown in Figure 30.24. It consists of two inlets through which species 1 and 2 (square boxes in Figure 30.24), respectively, can enter, an internal loop of three connectors and one outlet connector. The structure of this network is given in Table 30.19, which shows, according to the nomenclature of Figure 30.25, the number of each connector (plain numerals in Figure 30.24), the numbers of the two nodes associated with it (circled numerals) and the connectors which are common to the nodes. The connectors which can be closed by valves, in this case all the connectors, are shown by a valve symbol. Thus, for example, the last entry in the table states that the two ends of connector 6 have been denoted as 3 and 2, that connectors 3 and 5 join at node 3 and connectors 2 and 4 at node 2, and that connector 6 can be closed by a valve.

A proposed valve sequence is shown in Table 30.20. The authors give an analysis of the consequences of carrying out this sequence. The essence of the method is the use of symbolic logic to determine the consequences of proposed operations such as those put forward in Table 30.20.

30.43.4 Valve operations: Rivas and Rudd planner

The second, more difficult, problem in this work is the synthesis of safe valve sequences, considered by Rivas and Rudd (1974). This may be used to generate sequences for incorporation in operating instructions or to carry out real-time automatic sequencing.

Figure 30.26 shows another simple network of connectors. The system is filled with air and the objective is to initiate flow of hydrogen to the low pressure outlet without allowing hydrogen and air to come into contact under pressure.

The method is based on defining a hierarchy of successively more explicit goals, as shown in Table 30.21. Level 0 contains the overall goal; Level I goals are tasks, ordered to satisfy the Level 0 goal; and Level II goals are at the cause and effect level and are expressed as logical propositions. The objective is to get the computer to accept some intermediate level goal and then itself to synthesize the sequence. In this work the goals at Levels 0, I and II were created manually whilst the valve sequence was synthesized by the program from the Level II goals.

The planner used by Rivas and Rudd does not itself use a hierarchy of goals but is of the non-subgoaling type. It proceeds by adding actions in the order in which they will be executed. This facilitates checking to avoid unsafe states.

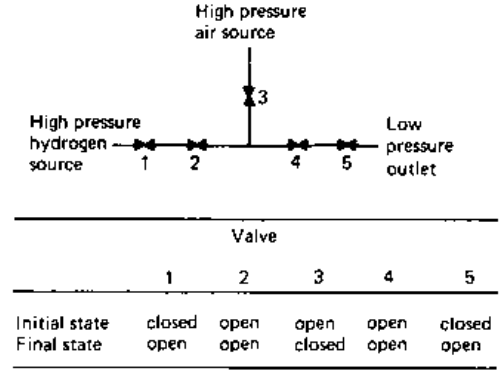


Figure 30.26 *Valve operations synthesis: second network of connectors (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Table 30.21 *Design of valve sequencing operations: hierarchy of goals for synthesizing valve sequences for second network of connectors (Rivas, Rudd and Kelly, 1974) (Courtesy of the American Institute of Chemical Engineers)*

Level 0 goal	*Level I goal*	*Level II goal*	*Valve operation*
Initiate hydrogen flow to low pressure outlet	Evacuate air	Stop air flow	Close 3
		Open system to low pressure outlet	Close 5
	Initiate hydrogen flow		Open 1
Final sequence (close 3, open 5, open 1)			

In order to limit the search space, the heuristic is adopted that an action is not considered unless it contributes immediately to the achievement of a goal. In other words, the planner looks only one step ahead. The planner uses forward chaining without backtracking.

As indicated earlier, this type of planner architecture is well adapted to the avoidance of unsafe states. On the other hand, the translation of high level into low level goals has to be done manually and the planner does not handle combinations and interactions of actions.

30.43.5 Operating procedures: Fusillo and Powers planner

Fusillo and Powers (1987) have extended the work of Rivas and Rudd to the synthesis of operating procedures in general. In this work procedure synthesis is represented as a state space and operators are used to move between states. A state is a vector of physical quantities such as flow, temperature and pressure, and of statuses of equipment such as valves and pumps. An operator represents the manipulation of equipment such as opening or closing a valve.

Salient features of the method are (1) system decomposition, (2) modelling, (3) constraints and (4) planning. These are now considered in turn.

System decomposition and stationary states

A system decomposition is sought which minimizes the interactions between the subsystems. In the approach adopted, a subsystem is one or more major process units, is physically isolable and, preferably, has stationary states.

A stationary state is essentially a quasi-steady-state condition. An example is a distillation column operating under total reflux. Stationary states are stable intermediate states and are invaluable in planning operating sequences.

For a continuous plant, one start-up strategy is to establish the stationary states of the subsystems with the pathways between them closed and then to integrate the subsystems to obtain the desired plant operating state.

Modelling

For each subsystem a set of global variables is defined. Each unit in the subsystem is modelled in terms of lists of effects which operations of the unit have on the variables in the subsystem. These effects are expressed in terms of a set of multiple discrete values (zero, low–low, low, medium–low, medium, medium–high, high, high–high). To aid planning, each unit type is designated as a source or sink of one or more variables. For example, a heat exchanger may be marked as a source of temperature, or a compressor as a source of flow.

Constraints

Constraints arise from a number of factors. The authors list (1) pre-conditions of unit operations, (2) requirements for a reaction, (3) production requirements, (4) hazards and (5) materials of construction. Use is made of both global and local constraints. A global constraint applies throughout the system. For example, there may be a constraint that two substances which can give an explosive mixture should not be allowed to mix. A local constraint is a pre-condition for some process task. For example, a fired heater should not be started up unless there is flow through the tubes.

Planning

Planning is effected by identifying the conditions which must be changed by the operating procedures, translating the identified changes into tasks, and ensuring that the proposed sequence of tasks will achieve the overall goals.

The planning method used is a modified means–ends analysis. Differences between the current state and the final goal state are computed. A set of intermediate goal states is formulated to reduce the difference between the current state and the final goal state. Movement from one state to another is effected by the application of operators, which are manipulations of units in the subsystems.

Planning proceeds in a hierarchical fashion. For example, the task of starting up a compressor has beneath it in the hierarchy the tasks of starting the seal flush and lubricating oil units. The planner takes an unordered list of manipulations, selects manipulations to achieve the goal and attempts to order the manipulations, using a depth-first search to effect the ordering.

The planning therefore utilizes three main strategies to reduce the search space: (1) constraints, (2) a hierarchy of tasks and (3) stationary states.

Computer program

Fusillo and Powers describe a prototype computer program, POPS, which implements the planning method just described. The program is written in LISP. Use is

made of a model library structured in the form of an is-a hierarchy.

Illustrative example
A chlorination plant is used by the authors as an illustrative example of the application of the planning method.

Actions, interactions and unsafe states
The planner of Fusillo and Powers (1987) is characterized by Soutter (1993) as one which attempts to separate action generation and action ordering. It first uses means–ends analysis to generate all the necessary actions and then uses a search to order these actions. Soutter classifies this as a non-subgoaling planner. For such a planner a difficulty is presented by interactions. This is so despite the attempts of the planner, described above, to minimize such interactions.

Fusillo and Powers (1988b) have addressed the problem of interactions. When failure of the plan occurs, new actions are added. However, this modification means that actions are no longer added to the plan in the order in which they will be executed, which means that it is no longer so easy to check for unsafe states.

30.43.6 Purging operations: Fusillo and Powers planner

Another valve operations problem addressed by Fusillo and Powers (1988a) is the synthesis of purging procedures. In purging it is necessary to consider each species separately. Features of a purging procedure are (1) the purging fluid, (2) the purging method and (3) the destination of the fluid purge.

The general approach adopted resembles that used in the authors' work on general operating procedures, as described above, in that it involves goal formulation, operator generation and task sequencing. There are, however, certain differences which arise due to the nature of the purging problem. For goal formulation, it is not always possible to discover intermediate goals by the computation of differences as in a normal means–ends analysis. In such cases an alternative method is used which involves the discovery of goals by analysis of the global constraints.

For operator generation, the operators consist of subsystem-wide purge operations. The authors give as an illustrative example the synthesis of a purge sequence for a chloroform reaction system.

30.43.7 Valve operations: Lakshmanan and Stephanopoulos planner

Further work on the synthesis of valve operations has been described by Lakshmanan and Stephanopoulos (1988a,b, 1990).

Lakshmanan and Stephanopoulos (1988a) review the state of planning in AI with particular reference to non-linear planning and to planning operators. They examine the problem of planning for operations such as valve sequencing and identify as a crucial problem that of the operators to be used. They consider the use of the STRIPS-style operator, which has a single set of pre-conditions and a single set of post-conditions, and rehearse its limitations. Such an operator cannot handle the situation in process plants where the post-conditions tend to depend on the state of the plant prior to application of the operator. They consider instead the functional operator, which has a number of sets of pre-conditions and of post-conditions such that a particular set of post-conditions is associated with a particular set of post-conditions. However, they suggest that using functional operators renders planning intractable.

In this and subsequent work, Lakshmanan and Stephanopoulos (1988b, 1990) describe a non-linear planning method based on hierarchical modelling and utilizing domain-specific knowledge. In this method planning proceeds in two principal phases: (1) problem formulation and (2) plan synthesis. The problem formulation phase involves (1) initial state description, (2) goal state description, (3) specification/identification of constraints, and (4) specification/identification of stationary states. The plan generation phase involves (1) identification of primitive operations, (2) construction of a partial plan and (3) synthesis of complete plans.

The approach adopted is domain-specific and utilizes a hierarchy of models. At the first, and lowest level, are the system variables and parameters. Each variable or parameter is formally defined as a collection of structured knowledge with attributes such as current value, current trend, range of values, etc. At the second level are the process 'streams', which include flows of mass, energy and momentum. The third level consists of constraining relationships such as mass, energy and momentum conservation, flow–pressure drop relations, and so on. The fourth level is the constraining relationships of the sets of defined process operating conditions. There is a corresponding hierarchy of structures, starting at the bottom with models of actual and notional ports, and rising through models of composite segments, of process units, of processing segments and of the complete plant. Planning then involves the identification of operators, their application to produce partial plans and a process of generate-and-test. The authors give as an illustrative example a catalyst regeneration problem.

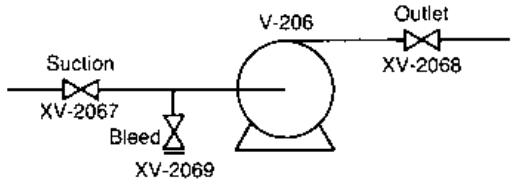
In that it solves valve sequencing operation by the use of domain-specific knowledge, the program is not a general OPS planner. This planner also is characterized by Soutter (1993) as a non-subgoaling planner.

30.43.8 Valve operations: planner of Foulkes *et al.*

Another study of this kind is the work on valve and pump sequencing carried out by Foulkes *et al.* (1988). The authors begin with a statement of the OPS problem. In a typical process system there may be a very large number of potential paths and thus a very large search space. Furthermore there are then likely to be a large number of solutions which are nearly, but not quite, correct.

They give a formal treatment of the combinatorial explosion problem and illustrate it by considering the plant used in the work of Rivas and Rudd (1974), in which the number M of on–off valves was 17. The number of different combinations of valve state is thus $2^M = 131\,072$.

Foulkes *et al.* argue that where the number of potential valve changes is large, the prior formulation of operating sequences for infrequently performed operations is not practical and is not attempted. The purpose of the work was to devise a system which could be used



(a)

```
Close suction valve XV-2067
Wait until pressure of V-206 pressure (PI-2065)
  is medium (less than 35 psig)
Stop compressor (SW-2066)
Confirm current through meter M-2066 zero
Close discharge valve XV-2068
Open bleed valve XV-2069
Wait until pressure of V-206 is zero
Close bleed valve XV-2069
```

(b)

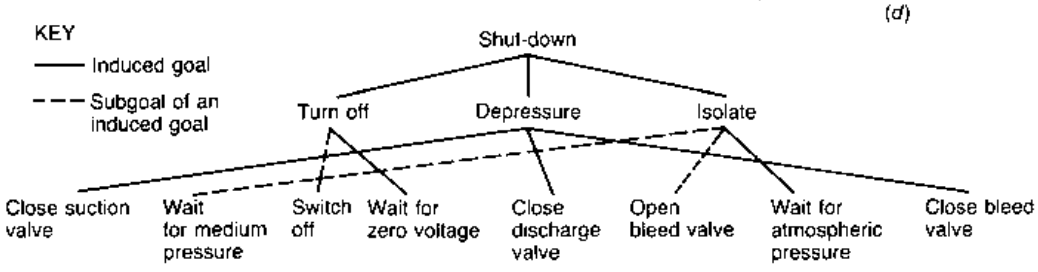
```
frame(compressor isa machine).
instance(V-206 isa compressor.
  [PressureGauge is PI-2065.
  Switch is SW-2066.
  Meter is M-2066])
```

(c)

```
operator DoShutdown
{
  compressor ?c;

  expand
   - shutdown of ?c is true
  using
    pressure of ?c is atmosphere;
    isolated of ?c is true;
    turned_off of ?c is true;
  end
}
```

(d)



(e)

```
operator CheckIdle
{
    compressor ?c;

    achieve
     - checkidle of ?c is true;
    using
      state of ?c is off;
    end

    print
      'Confirm the current through meter:
      (?m) [Meter of ?c is ?m;] 'is zero';
}
```

(f)

Figure 30.27 *Operating procedure synthesis: shut-down of a compressor (Soutter and Chung, 1995b): (a) Compressor system V-206; (b) steps in shut-down sequence (after Sutton, 1992); (c) definition of compressor V-206 as an object; (d) hierarchical operator DoShutdown; (e) translation of high level goal into low level goals; (f) planning operator CheckIdle*

off line to devise on demand a suitable sequence for a particular operation.

They describe a method in which the plant is decomposed into the elements 'pipe fragment' and 'pump fragment', which consist of a piece of pipe with a valve or a pump, respectively, on the end. Planning proceeds by searching first for paths and then for sequences of valve and pump operations, subject to constraints.

The program was written in Prolog and illustrates the

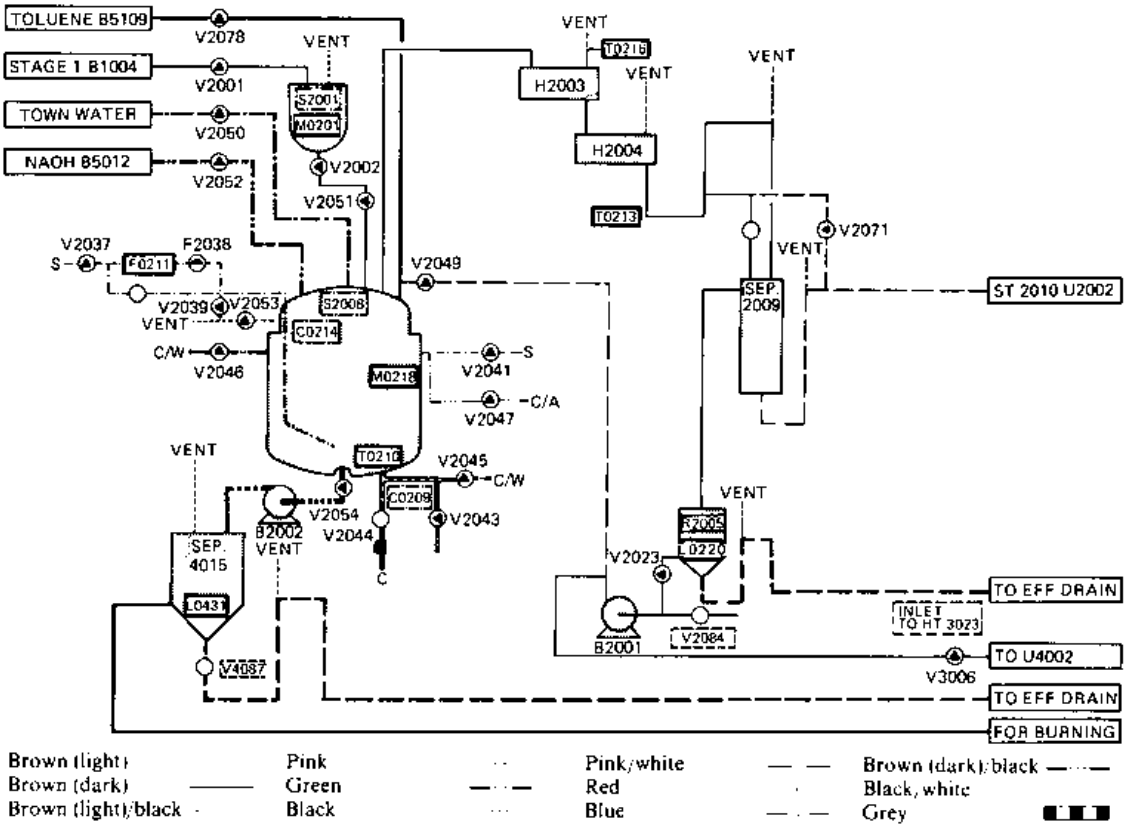


Figure 30.28 *Computer graphics displays of system state – mimic diagram (The Boots Company Ltd). In the original display full use is made of colours. Coloured pipe lines in the original are shown in the above figure according to the code shown*

exploitation of the facilities of that language for declaring 'operators', for 'pattern matching' and for depth-first search.

30.43.9 Operating procedures: Soutter and Chung planner

An attempt to develop a general-purpose method OPS known as the Chemical Engineering Planner (CEP), is described by Soutter and Chung (1995b). This planner is intended to perform both general OPS tasks and valve operations synthesis.

CEP is a hierarchical planner. It receives higher level goals and translates them into lower level goals. The planning engine is complemented by an inference engine, which performs the goal translation just described. This inference engine uses backward chaining. CEP is believed to be the first planner to use both types of engine.

CEP is described as a STRIPS-based planner, apparently primarily in recognition of its use of STRIPS-type operators. The planning engine in CEP, however, follows the strategy of least commitment, utilizing partial ordering. In other words, CEP is a non-linear planner. These two features of CEP, backward chaining and non-linear planning, keep it compatible with the main thrust of development in AI planning.

The planner in CEP is assisted by 'agents' which perform various specialist functions. One agent monitors conflicts, another advises on complex goals, and so on.

The problem of unsafe states is handled in CEP in terms of global constraints. A global constraint is a set of unsafe states. Goals of prevention are used to prevent entry into an unsafe state.

CEP utilizes a problems specification language. This language describes four types of knowledge: (1) the domain objects, (2) the operators, (3) the global constraints and (4) the problem specification.

The inference engine utilizes inference operators. For example, the high level goal *flow(inlet, outlet)* is the establishment of flow from inlet to outlet of a pipe. This is translated by the inference engine using the appropriate inference operator into the lower level goals *open(inlet, middle)* and *flow(middle, outlet)*. The latter is further translated in a similar way. The relevant inference operator is:

```
operator FindFlow
(
 pipe?a; pipe ?b
```

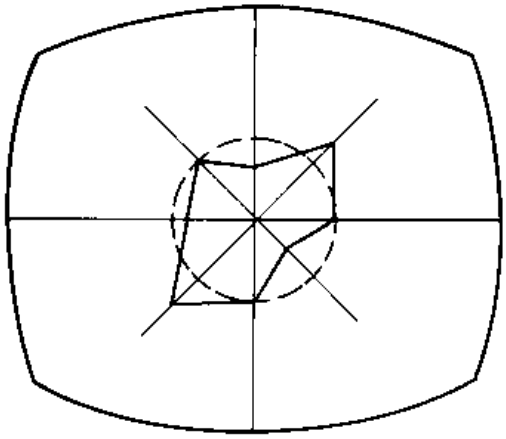


Figure 30.29 *Computer graphic displays of system state – polar plot (after Wolff, 1970) (Courtesy of the Scientific Instrument Research Association)*

```
pipe ?c;

expand
*flow(?a, ?b)
using
    open(?a, ?b)
    flow(?c, ?b)
end
)
```

In some cases an inference operator which defines a hierarchy is termed a hierarchical operator.

As an illustration of planning using CEP, consider the problem of the start-up of a compressor described by I.S. Sutton (1992), in an account of the writing of operating instructions. The problem may be explained by reference to Figure 30.27. Figure 3.027(a) shows the compressor V-206 itself. The task set is to shut down compressor C-206. Figure 30.27(b) shows the steps in the shut-down sequence given by Sutton.

For the planner the task is to achieve the goal *shut-down of V-206 is true*. Figure 30.27(c) shows the definition of V-206 as an object. Figure 30.27(d) shows a typical hierarchical operator *DoShutdown*. Figure 30.27(e) shows the translation of the high level goal into the lower level, or induced, goals. Figure 30.27(f) shows a typical planning operator *CheckIdle*.

The operation of the planner is indicated by the following brief outline. The goal is *shut-down of V-206 is true*. This goal is translated by the inference engine using the hierarchical operator *DoShutdown* into the three subgoals:

(1) pressure of V-206 is atmospheric;
(2) isolated of V-206 is true;
(3) turned-off of V-206 is true.

The planner selects the first subgoal and proposes the addition to the plan of the action Depressure. The corresponding operator has the pre-conditions

(1) pressure of V-206 is medium;
(2) bleed of V-206 is open;

and the effect

(1) pressure of V-206 is atmospheric.

However, if this action is entered as the start of the plan, a global constraint is violated. This global constraint is that the bleed valve should not be open when the compressor is on. This constraint is violated because the initial state is that the compressor is on. In order to prevent violation a new action is added to switch off the compressor before the action *Depressure* is taken.

The OPS output given by the planner is essentially the same as that shown in Figure 30.27(b).

30.43.10 Operation procedures network

Most work on OPS is based on a component oriented approach. Work utilizing instead Forbus' qualitative process theory (QPT) has been described by Rotstein,

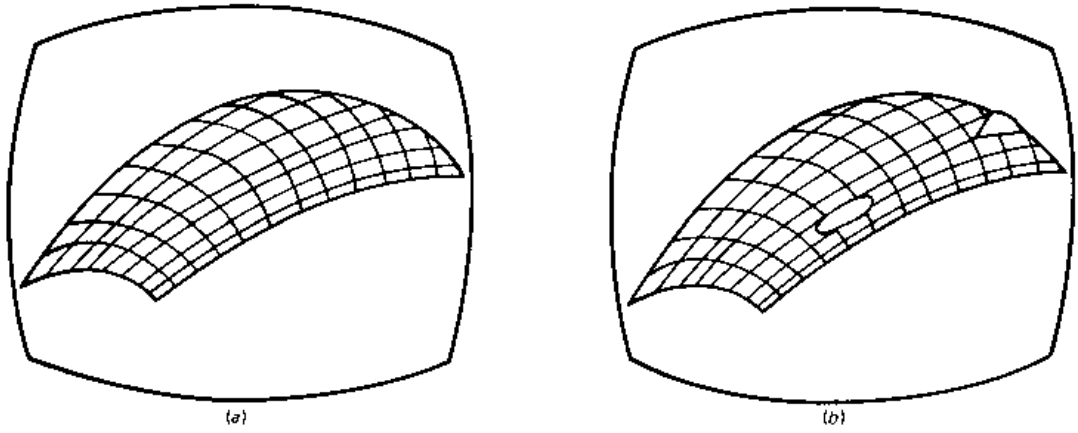
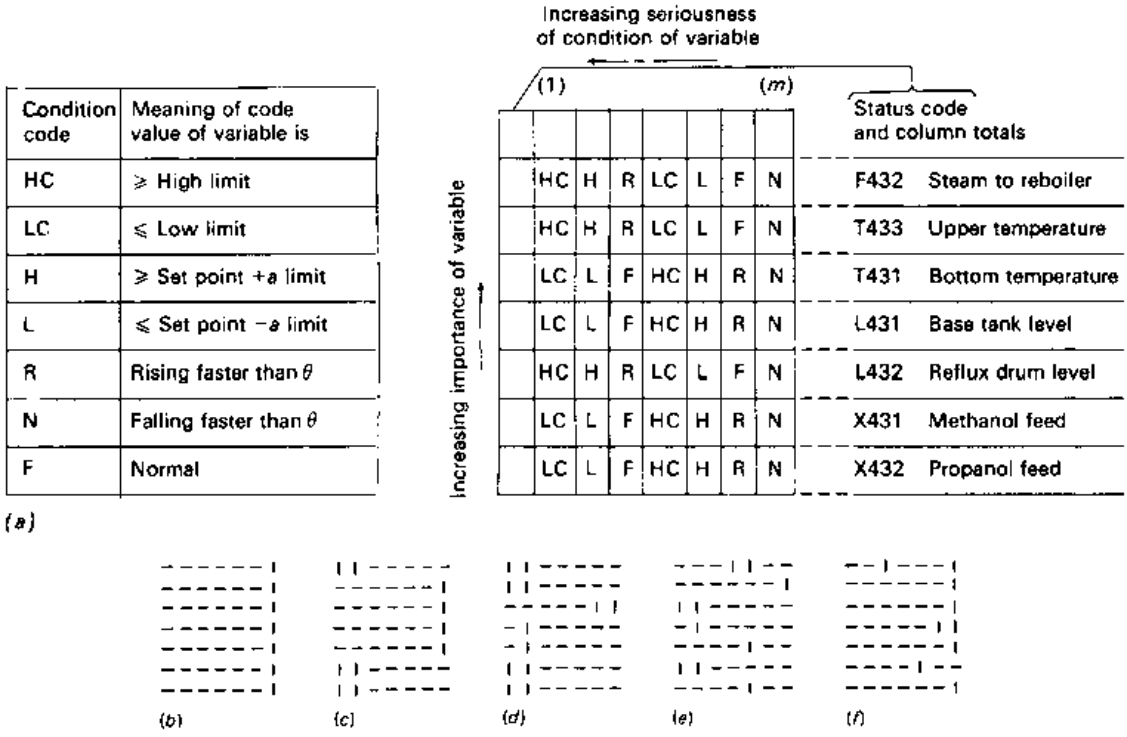


Figure 30.30 *Computer graphic displays of system state – surface plot (after H.H. Bowen, 1967): (a) normal condition; (b) abnormal condition (Courtesy of Taylor & Francis Ltd)*



Condition code	Meaning of code value of variable is
HC	⩾ High limit
LC	⩽ Low limit
H	⩾ Set point +*a* limit
L	⩽ Set point −*a* limit
R	Rising faster than θ
N	Falling faster than θ
F	Normal

Figure 30.31 *Computer graphic displays of system state – status array (Stainthorp and West, 1974): (a) key to status array; (b) normal operation; (c) severe upset condition; (d) shut-down necessary; (e) clear for start-up; (f) near-normal operation (Courtesy of the Institution of Chemical Engineers)*

Lavie and Lewin (1992), who propose the concept of an operation procedures network (OPNet).

The motivation for this approach is the deficiencies of the component based method in the treatment of batch processes. QPT lends itself better to the handling of the basic transformations of mass and energy in such processes.

The method described by the authors involves the following stages: (1) the definition and ordering of the mass and energy balances, (2) their instantiation in a particular plant structure, (3) their ordering in space and time and (4) the synthesis of the operating procedures.

30.44 Process Monitoring

Process monitoring has several aspects. One is the detection of a disturbance or abnormality which falls short of an identifiable fault and which does not necessarily result in any process alarm. The second is the handling of alarms caused by some fault or operator action, the diagnosis of the fault and the response to it. The third is the detection of a incipient malfunction which has not yet resulted in a fault or an alarm. There are advanced methods, including AI techniques, which address all three of these. The first aspect is considered in this section and the others in the two subsequent sections. An overview of some of the methods available for these functions is given in *Fault Detection and Diagnosis in Chemical and Petrochemical Processes* (Himmelblau, 1978).

30.44.1 Disturbance characterization

One form of monitoring which is in widespread use is data reconciliation. It is important for process operation to have a valid mass and energy balance. Factors such as process transients and measuring instrument errors mean that it is not a trivial matter to obtain such balances.

Data reconciliation is able to draw on a large body of work on estimation and filtering, and some form of data reconciliation is quite common practice. Quite separately from this, the process operator monitors the process and comes to a judgment as to whether it is in a normal condition or whether there is a disturbance or abnormality. In doing this he makes use of his mental model and of heuristics such as limit, or landmark, values and rules of thumb.

There is now emerging a formal approach to the interpretation of process information. Thus Cheung and Stephanopoulos (1990) have described a methodology for transforming the information given by trend records into indicators of process state which are sufficiently quantitative to allow the operator to make powerful inferences about trends in variables which are not measured.

Some of the difficulties faced by the process operator in interpreting process information are enumerated by Cheung and Stephanopoulos. Some causes of these difficulties are that there may be (1) process outputs changing at different rates, (2) dead time and inverse responses, (3) interactions between control loops, (4) conflicting information from sensors, and (5) incomplete information due to 'lost' sensors. The operator may therefore find it have difficult to (1) distinguish between normal and abnormal conditions, (2) assess current trends and anticipate future states, (3) identify the causes of these trends and (4) plan and schedule sequences of operating steps leading to a new operating level.

Another approach is that described by Whiteley and Davis (1992). These authors treat the problem in terms of adaptive pattern recognition and develop a qualitative interpretation of the process information.

30.44.2 Trend and state display

Turning to displays of the process trends and state, computer graphics have made it possible to create displays which previously could not be contemplated. The starting point for the design of such displays should be a consideration of the operator's tasks and problems, and a display should evolve as a solution to these. Otherwise there is a danger that the display will be a solution looking for a problem. Various types of display have been developed by computer manufacturers for loop parameters, trend records, etc.

Display of system state is one of the most important types of display. Some illustrative examples of this type of display are given in Figures 30.28–30.31.

Figure 30.28 represents a mimic diagram. This particularly display is simply a colour slide which the operator uses to help him identify equipments. VDU displays can be provided on similar lines with continuous updating of equipment status.

Figure 30.29, after Wolff (1970), shows a polar plot of eight variables in which the length of each vector is proportional to the measured value. The vectors are scaled so that at the normal values their tips touch a common circle. Figure 30.30, after H.H. Bowen (1967), illustrates a rather similar principle in which the variable vectors are scaled to form a common surface, Figure 30.30(a) showing a normal condition and Figure 30.30(b) an abnormal one. Figure 30.31, after Stainthorp and West (1974), shows a status array for a distillation column with methanol and propanol feeds. The rows represent process variables and the items in them absolute, deviation and rate-of-change alarms or the normal condition as shown in Figure 30.31(a). Figures 30.31(b)–(f) correspond to the conditions normal operation, severe upset, shut-down necessary, clear for start-up and near-normal operation (during start-up), respectively.

Displays have been described for facilities such as manual control (e.g. Crawley, 1968), scheduling (e.g. Ketteringham, O'Brien and Cole, 1970; Ketteringham and O'Brien, 1974), etc. Other displays for activities such as malfunction detection are described below.

The degree of sophistication in the information processing underlying a display varies greatly and may not be apparent from the display itself. Thus the polar and surface plots illustrated above require only scaling of the measurements, while other displays involve the use of predictive models, estimation techniques, etc.

30.44.3 Multi-media aids

Another development is the use of multi-media aids which exploit the potential of combinations of audio, visual and other forms of information presentation. Accounts are given by Alty and McCartney (1991) and Alty and Bergan (1992).

The approach taken in this work to use multi-media aids under the control of a knowledge based system. Some media which are used in such work include: text, static graphics and diagrams, dynamic graphics, animation, sound, speech and video. There is a wealth of research available in the human factors literature on the relative efficacy of different media for the transmission of different types of information.

A system which uses alternative media needs to be supported by a resource management facility which selects and schedules the media. In the work described, use is made of a knowledge based system for this purpose.

There is no lack of options for the design of such a system, but it is still early days in the development of the principles which should govern such design. Alty and Bergan (1992) have described a laboratory study involving the Crossman water bath experiment on manual control with multi-media aiding. Experiments on the use of multi-media facilities in industrial process control rooms have been conducted and the reception is said to have been favourable.

30.44.4 Expert systems

There are also developments in the application of expert systems to process monitoring. There is a considerable monitoring element in the expert systems for process control described in Section 30.35. In some expert systems, however, assistance to the process operator in assimilating process information is the prime aim. An example is ESCORT, described by Sachs, Paterson and Turner (1985).

30.45 Fault Administration

The second aspect of process monitoring is fault administration. One of the principal functions of a computer system in process control is to assist the operator in the handling of fault conditions. The use of the computer to enhance the alarm system has been described in Chapter 14. Among the enhancements mentioned there are systems in which alarm diagnosis, or alarm analysis, is performed. In those early systems the alarm diagnosis facilities provided were fairly basic and the data structure for the diagnosis was created manually. Since then a good deal of work has been done on alarm diagnosis systems which have more advanced facilities and in which the alarm data structure is generated automatically.

The bulk of the work on fault administration has been concerned with alarm handling and diagnosis, although there is some work on other aspects such as on advice for corrective actions and on prediction times at which excursions across alarm limits will occur.

Fault administration has proved particularly attractive to workers in AI and expert systems. For example,

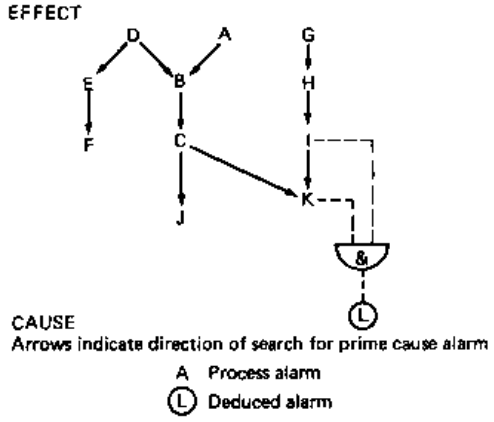


Figure 30.32 *Alarm tree including a deduced alarm (Andow and Lees, 1975) (Courtesy of the Institution of Chemical Engineers)*

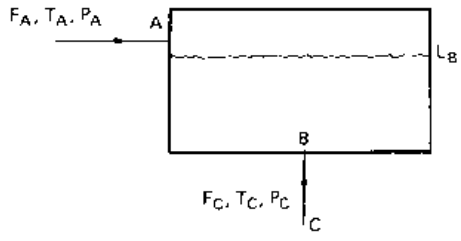


Figure 30.33 *Mixing tank system (Andow and Lees, 1975). Functional model equations: $dL_B/dt = f(F_A,F_C)$; $dT_C/dt = f(T_A,L_B,F_A)$; $P_A = f(T_C,L_B)$; $P_B = f(P_A,L_B)$; $F_C = f(P_B,P_C)$ (Courtesy of the Institution of Chemical Engineers)*

estimates of the proportion of applications of process industry expert systems which are in this field range from some one-third to one-half.

A number of distinct phases may be discerned in work on alarm handling and diagnosis: (1) manual design of alarm analysis systems for industrial nuclear power stations; (2) early explorations of the systematic creation of the alarm data structure; (3) disturbance analysis systems, prompted by the Three Mile Island accident; (4) expert systems; and (5) various AI approaches, notably those based on modelling and on neural networks. A review of developments to the third of these phases has been given by Lees (1983c).

Fault administration is another field where qualitative modelling, including fault propagation modelling, plays a central role in many of the methodologies developed.

30.45.1 Alarm structure and display

Before describing some of the advanced aids developed for handling alarms, it is pertinent to consider the quality of the basic alarm system provided. It makes little sense to draft a sophisticated alarm diagnosis system onto a fundamentally defective alarm system design. Two aspects of this design are of particular relevance. One is the structure of the alarms and the other their display.

The issue of the structure of the alarm system has been addressed in several different ways. Some of these take as their starting point failures and others take the resulting undesirable events. Thus one approach is to list the faults which it is desirable to be able to identify because they are in some way significant, and to assess the ability of the system to give an unambiguous indication that a particular fault, and no other, has occurred. In other words, an assessment is made of the degree of fault discrimination. The problem is akin to that of the observability of process variables. Work in this area has been described by Park and Himmelblau (1987).

Another approach, described by Lambert (1977) and based on his concept of the probabilistic 'importance' of the events in a fault tree, is to create fault trees for the principal undesired events on the plant and to identify in each tree measurable events which rank high in importance.

The approach taken by Modarres and Cadman (1986) is not dissimilar, but centres rather on the effectiveness of the alarm system in supporting the activities of the process operator. The method described is based on the use of goal trees for the operation of the plant and of decision trees, which can be constructed in parallel to show all the operator actions required to achieve each goal and also the consequences of failure to achieve the goal.

These various approaches are not, of course, mutually exclusive.

30.45.2 Alarm trees

Work on alarm diagnosis for process plants took as its starting point the use of alarm handling systems in nuclear plants, described in Chapter 14. Thus Welbourne (1965, 1968) gives an account of the use of alarm trees. A simple alarm tree is shown in Figure 30.32. The alarm tree gives the relations between process alarms, and does so economically without duplication of information. There is no emphasis on any particular top event. Deduced alarms may be added to the tree, but the tree is self-sufficient without them.

Early work on alarm diagnosis for process plants was done by Andow and Lees (Andow, 1973; Andow and Lees, 1975) and Powers (1975). Andow and Lees explicitly took the view that alarms diagnosis was likely to find a role on process plants only if the necessary knowledge base could be created with reasonable economy, and that this knowledge base should consist primarily of models rather than rules.

They describe a method for creating the alarm data structure based on fault propagation models of the type described in Section 30.36. The flow diagram is converted into a block diagram of linked unit models. The models used are simple functional models such as that of the mixing tank shown in Figure 30.33. This representation is then converted into a network of interacting process variables, effectively a digraph, and this network is then reduced to the network of those process variables on which there are alarms. The method utilizes list processing to produce the alarm network automatically from the unit models. Figure 30.34 shows two alarm trees for the mixing tank system. Whereas the

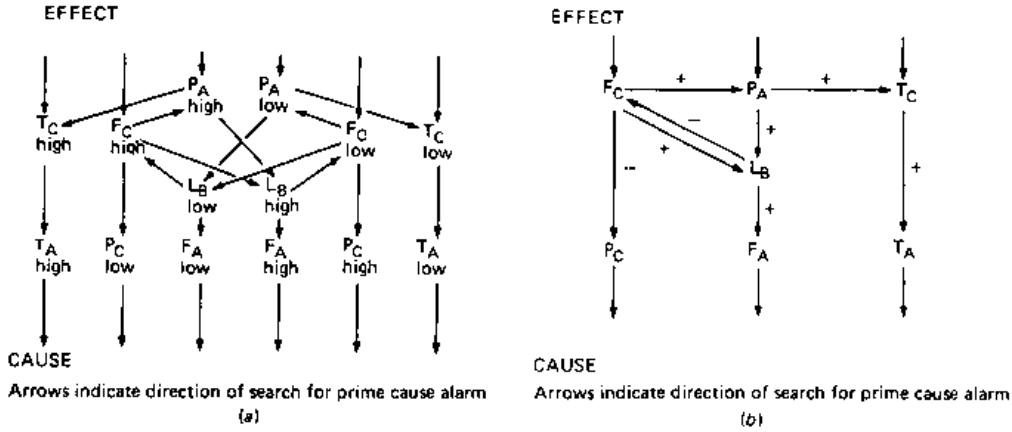


Figure 30.34 *Alarm trees for mixing tank system (Andow and Lees, 1975): (a) conventional alarm tree; (b) process variable-based alarm tree (Courtesy of the Institution of Chemical Engineers)*

Table 30.22 *Modified 'truth table' containing probabilities for a deduced alarm (Andow and Lees, 1975) (Courtesy of the Institution of Chemical Engineers)*

Process alarms and their probability weightings									*Target value*	*Deduced alarm message*
A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*		
0.7	0.45	0.8	0.3	0.65	–	–	–	–	2.1	Fault X
0.3	0.75	–	–	–	0.9	0.8	–	–	1.85	Fault Y
–	0.2	0.45	–	0.65	0.7	–	0.65	0.3	1.75	Fault Z

conventional alarm tree is as shown in Figure 30.34(a), the alarm tree obtained by this method is that given in Figure 30.34(b).

The type of display envisaged by Andow and Lees is illustrated in Table 30.22, which is a form of truth table. In a conventional truth table an active alarm is TRUE and an inactive one is FALSE. The truth value of deduced alarm X depends on the truth values of the set of process alarms. This deterministic approach may be replaced by a probabilistic one, as used in Table 30.22. In this table the evaluation TRUE is obtained if the sum of the products of the process alarms A–I and the probability weightings exceeds the target value, active alarms having a value 1 and inactive ones 0. The normal truth table is a special case of this more general table.

30.45.3 Fault trees

Another early approach taken to the creation of an alarm data structure is the use of fault trees. A fault tree shows the relation between the top event, which is usually some hazardous condition, and the bottom events, which are typically mechanical faults. It tends to emphasize these top and bottom events. A separate fault tree is needed for each top event.

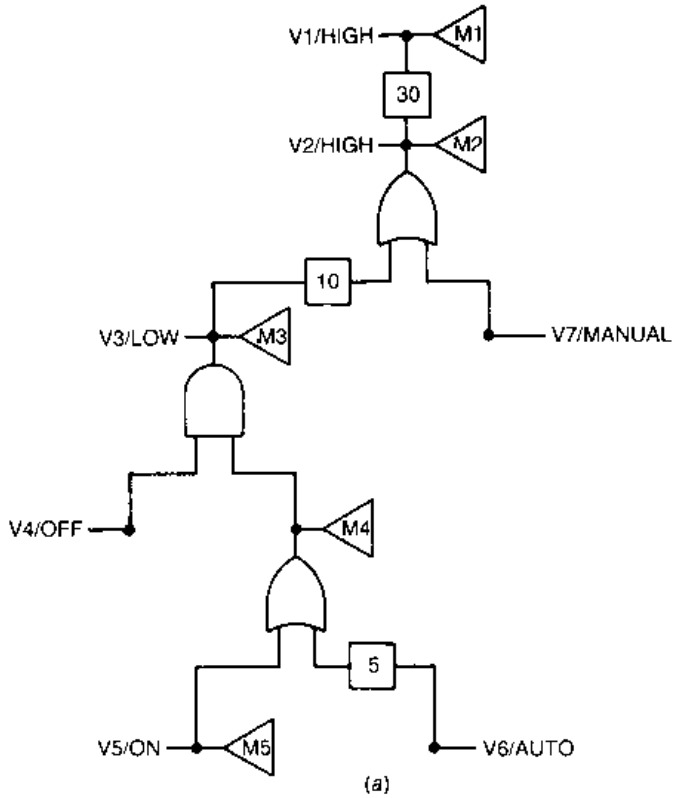
The use of alarm structures based on fault trees was suggested in early work by Powers and co-workers. An outline of an approach towards the synthesis of fault trees was been described by Powers and Tompkins (1974a,b), whilst Powers (1975) conducted experiments in which a fault tree was used to assist an operator to diagnose inert gas blanketing in a heat exchanger. The use of fault trees to create the alarm data structure was also investigated by Martin-Solis, Andow and Lees (1977). They used fault propagation models to derive mini-fault trees, as already described in Section 30.42, and obtained alarm structures essentially similar to digraphs containing AND gates. The work showed that the veracity of the instrument readings is a significant problem in computer alarm diagnosis, just as it is in human fault diagnosis.

This work on alarm diagnosis by Andow, Lees and co-workers was the origin of their work on fault propagation modelling, which has since found further application in hazard identification and fault tree synthesis.

30.45.4 Disturbance analysis systems

The accident in 1979 at Three Mile Island (TMI), described in Appendix 21, highlighted the importance of alarm systems and alarm diagnosis. The problems experienced by the operators led the task force to make recommendations for the use of a safety status display and for work to establish the feasibility of a disturbance analysis system (DAS).

TMI gave impetus to work in course at the Electrical Power Research Institute (EPRI), Palo Alto, California, described by Frogner and Meijer (1978, 1980), Long (1980), Long *et al.* (1980) and Meijer, Frogner and Long (1980).



(a)

Time (s)	Event	Result of the cause–consequence analysis
0	V4 = OFF and V5 = ON	M4 and M5 active M3 potentially active
1	V3 = LOW	M3, M4 and M5 active M2 potentially active
11	V2 = HIGH	M2..... M5 active M1 potentially active
41	V1 = HIGH	M1..... M5 active

*Initial conditions: $V_1 \neq$ high, $V_2 \neq$ high, $V_3 \neq$ low.

(b)

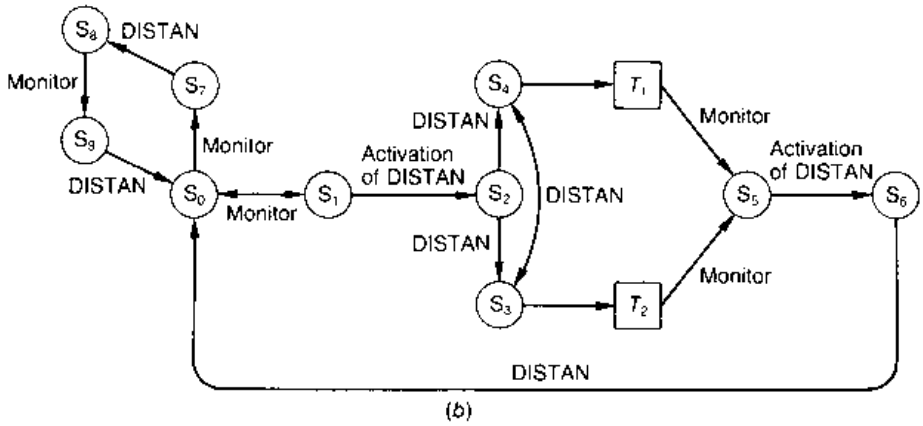
Figure 30.35 *Disturbance analysis system: conceptual example of a cause–consequence tree and of a sequence of events in the tree (Frogner and Meijer, 1980): (a) cause–consequence tree; (b) sequence of events (Courtesy of the Electrical Power Research Institute)*

An initial study was made of the potential benefits of a DAS. The assessment was made by selecting suitable nuclear power station subsystems, obtaining data on the outages of these subsystems in existing stations, and estimating the proportion of these outages which would probably have been avoided using a DAS facility. An initial survey showed that out of 1161 outages there were 274 which appeared preventable by more rapid action aided by a DAS. These authors subsequently did work with an experimental DAS which showed appreciable reductions in operator response time between the two cases where the DAS was not used and where it was.

Long gives an analysis of some of facilities that a DAS might provide. It could upgrade the plant signals and

S_0	Normal condition: variable is within its specified limits
S_1	Value was within limits and it just went outside
S_2	Disturbance analysis is currently performed due to S_1
S_3	Analysis due to S_2 is complete: cause not known
S_4	Analysis due to S_2 is complete: cause known
S_5	Value was outside limits and it just went inside
S_6	Disturbance analysis is currently performed due to S_5
S_7	Too high a frequency of events has been registered for this variable. Analysis is being performed or waiting on DAS
S_8	Variable causing spurious events
S_9	Spurious event causing variable becomes normal. Analysis is being performed or waiting on DAS
S_{10}	False event

(a)



(b)

Figure 30.36 *Disturbance analysis system (Frogner and Meijer, 1980): (a) status indicators; (b) state transition diagram for status indicators. DISTAN denotes Disturbance Analyser (Courtesy of the Electrical Power Research Institute)*

infer important parameters from simple analytical models, could monitor the mode of operation and compare the configuration with simple plant configuration models, and could recognize disturbances and provide assistance with procedures for off-normal conditions.

The DAS developed in this work utilizes a multi-level methodology. Level 1 is based on decision tables, the inputs to a table being one or more sensor signals and the output a message. Level 2 utilizes the cause-consequence tree (CCT) method. Level 3 provides a facility for the use of quantitative models.

The Level 1 decision tables are relatively simple and serve to reduce the proportion of signals passed on to Level 2. The more complex signal patterns are analysed in Level 2 using the CCTs. The general form of the CCTs and the terminology used are shown in Figure 30.35. The tree in Figure 30.35(a) consists of nodes connected by arcs, the nodes being associated with attributes. These attributes are a variable identifier (V1, V2,...), a required condition for the variable (HI, LO,...), a message identifier (M1, M2,...), a logic gate (AND, OR,...) and a time delay (5 s, 10 s,...).

The methodology defines a node as observable if it associated with a variable measured by a sensor. An observable node is given a required condition. If this condition is met, the node is active. A time delay is the expected minimum time between two events. If the observed time between two events is less than the time delay, or if the observed sequence does not correspond to that in the tree, it is assumed that the branch is not active. The use of time delays, therefore, contributes to the unique identification of a disturbance. If a node is active and it has associated with it a message, that message is also active. If a node is not active solely because the time so far elapsed is less than the time delay, the node and the associated message are

potentially active. A typical sequence of events for the CCT shown in Figure 30.35(a) is shown in Figure 30.35(b).

The status of a variable is shown by one of a set of status indicators. These status indicators are listed in Figure 30.36(a) and the state transition diagram for the indicators is shown in Figure 30.36(b). The normal value of a status indicator for a variable is S_0. If a value goes outside its limit, the indicator is set at S_1. When the disturbance analysis starts, the indicator is set at S_2. The result of a disturbance analysis causes the indicator to be set at S_4 if a satisfactory message is determined or at S_3 if the cause cannot be found. Once the value is outside its limits, this value is latched for a period of T_1 seconds for an S_4 variable or T_2 seconds for an S_3 variable. If the value returns inside the limit, it is set at S_5 once the latching period has elapsed. Again the disturbance analysis is actuated, but this time with low priority and the indicator is set at S_6. When the disturbance analysis is complete, the indicator is set at S_0. Status indicators S_7–S_9 and S_{10} are associated with algorithms which deal with spurious events and failure events, respectively. Methods are given for the treatment of faults on, and of temporary excursions of, sensors.

The data acquisition system (DAS) was tested on a training simulator and operated by process operators from nuclear power plants. In general, it behaved reasonably well, but the reduction in average operator response time from 34 to 30 seconds was not great. The time required for the operator to move physically to the appropriate part of the control room accounted for an appreciable fraction of the total response time in both cases.

A number of human factors points emerged during this work, of which just one may be quoted. Frogner and Meijer (1980) state:

> The DAS effectiveness is reduced if the results of the diagnosis are presented without adequately conveying the status of the process. For the operator to exercise judgement and not just function as an automaton, he must understand the state of the plant and the reason for his action. In this respect, the condensed one-line DAS messages need improvement. It is recommended that future systems incorporate DAS messages into a more informative picture of the state of the process; for example, by using process and instrumentation diagrams.

In this method, the CCTs are created manually by the analyst. Considerable effort was required to produce the model data base, which is plant specific, and this effort was seen as a factor limiting application.

Another major project on disturbance analysis which took place at about the same time was the joint project between the Gesellschaft für Reaktorsicherheit (GRS) at Garching, in then West Germany, and the Institut for Atomenergi at Halden, Norway, involving development of DAS systems known as STAR for the nuclear power plants at Grafenrheinfeld and Biblis in the former country.

As in the EPRI work the fault propagation is represented by cause-consequence diagrams (CCDs). Some of the differences between the EPRI and GRS systems have described by Frogner and Meijer (1978) and Bastl and Felkel (1981).

30.45.5 Expert systems

One of the modes of operation of the commercial expert system PICON, referred to above in Section 30.36, is the alarm management mode. Accounts of its operation in this mode have given by Berkovitch and Baker-Counsell (1985), R.L. Moore (1985) and Rand (1987). The latter describes the creation of the rule base by observation of operators, interviewing of operators and operator input of rules, with the latter being favoured.

An account of ESCORT, a system for detection and diagnosis of faults and the detection of instrument malfunction is given by Sachs, Paterson and Turner (1985).

Two large expert system projects FALCON (Shirley, 1987) and REACTOR (W.R. Nelson, 1982) on systems with large rule bases have been carried out and are reported to have had success in some applications.

An expert system based on EXPERT has been developed by Mizoguchi (1983). The application described is fault diagnosis on a nuclear reactor primary cooling system. The rule base consists of some 76 rules, of which 6 are finding-to-finding, 60 finding-to-hypothesis and 10 hypothesis-to-hypothesis rules.

In the expert system for malfunction diagnosis described by Shum *et al.* (1988), use is made of a hierarchical structure in which the nodes represent particular malfunction hypotheses. Use is made of the concept of 'specialists', a concept used also in the design language DSPL, referred to in Section 30.27. There is a collection of 'specialists' co-ordinated to arrive at an overall diagnosis. Each specialist possesses compiled and qualitative knowledge for the evaluation of a hypothesis. The method is claimed to be especially effective at handling multiple symptoms and multiple malfunctions.

There are a number of other systems which are described as expert systems, but which place emphasis on models as well as rules, as described below.

30.45.6 Model-based methods

Iri *et al.* (1979) have used digraph models to represent the alarm structure of a plant. This work has subsequently been developed in a number of studies, including those of Kokawa, Miyaki and Shingai (1983), Shiozaki *et al.* (1985) and Qian (1990).

An expert system MODEX for malfunction diagnosis has been described by Rich and Venkatasubramanian (1987), and its successor MODEX2 has been described by Venkatasubramanian and Rich (1988). The system is based on a two-tier architecture, consisting of a bottom level of process specific, compiled knowledge and a top level of process general, deep level knowledge. An agenda-based inference control algorithm generates malfunction hypotheses from structural and functional information about the process. Diagnostic reasoning alternates between the two levels.

Finch, Oyeleye and Kramer (1990) given an account of a program MIDAS which diagnoses the causes of plant disturbances, including equipment degradation and failure, sensor failure, incorrect operation and external disturbances. The diagnosis utilizes an event model to construct clusters of events, each cluster being associated with a single fault. The program handles features such as variations in order of detection, complex dynamics, sensor failures and multiple plant failures.

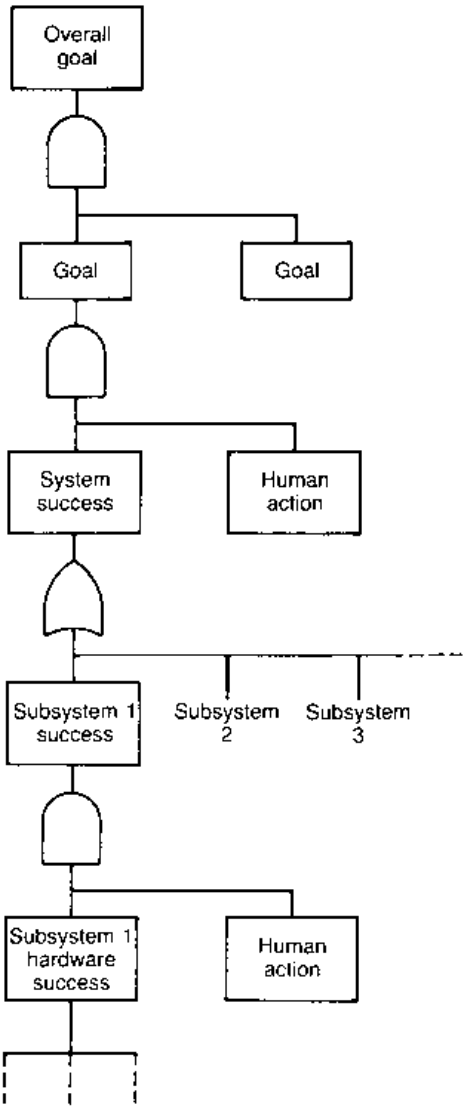


Figure 30.37 *A outline goal tree–success tree*

In the work of Ramesh, Shum and Davies (1988) the emphasis is on the nature of the tasks involved in diagnosis. One task is associated with the plant sensor and another with the product quality data. Ramesh, Davies and Schwenzer (1992) develop this approach, with an investigation of the information processing tasks underlying diagnostic reasoning.

The approach described by Grantham and Ungar (1990) differs from others in two main ways. It utilizes Forbus' qualitative process theory (QPT), and it can automatically modify the unit models, allowing identification of faults which significantly change unit behaviour. The authors characterize their method as one which operates at a higher level of generality, and hence robustness, by giving the system an ability to create its own models from a description of the substances and objects present and the prevailing process conditions. It has the ability to identify faults which change significantly the mode of operation of a unit, without the need for explicit fault modes.

A prototype expert system PRODES for fault diagnosis is described by Labadibi and McGreavy (1992). The system utilizes fault propagation models elicited from the user and cast in the form of decision tables.

Saelid, Mjaavatten and Fjalestad (1992) have described an expert system for operator support with object oriented features and utilizing an expert system shell. The system detects disturbances in the connections between units, identifies the faulty unit and then initiates diagnosis of that unit. This internal unit diagnosis utilizes a combination of process models, fault trees and Kalman filtering.

30.45.7 Fault-tree-based methods

Ulerich and Powers (1988) have described a method for fault diagnosis based on fault trees. This work extends the earlier work of Powers (1975) on this topic. It utilizes the FTS methodology for fault tree synthesis from digraphs developed by Powers and co-workers, as described in Section 30.41. A prior fault tree is created. From this prior tree there is then created a further fault detection tree in which there is attached to each basic event a verification; the event is treated as valid only if it is verified. The verification consists of a set of process indications which must all be satisfied.

30.45.8 Goal tree-success tree method

The expert system GOTRES for fault diagnosis is described by Chung, Modarres and Hunt (1989). The system is based on the goal tree–success tree (GTST) method illustrated in Figure 30.37. The tree is developed from the process objective at the top, downwards to successively lower levels of goal. Since all goals are necessary for success, the logic gates relating the goals are all AND gates. The nature of the tree changes at the point where it is no longer possible to develop the tree without reference to hardware. Attached to each goal is a goal verification procedure which uses relevant process indicators to determine whether the goal is satisfied.

The authors state that experience shows that the use of a success tree rather than a failure, or fault, tree allows a more succinct treatment. They also suggest that a success orientation corresponds better to human thinking, and illustrate this with the analogy of a car journey, where the driver concentrates on the success paths rather than the failure paths.

Chen and Modarres (1992) describe an expert system FAX for the diagnosis of faults and advice on corrective actions, with emphasis on the latter. The control objective is represented as a goal tree with success paths for both plant and operator inputs, and corrective actions are found by an adaptive search.

30.45.9 Neural networks

A quite different approach to alarm diagnosis is the use of neural networks, for which this appears a natural application, and a number of studies have been published.

Neural networks were described in Section 30.21. Most of the work on such artificial neural networks (ANNs) is concerned with back-propagation networks (BNPs). The studies done cover learning, recall and generalization.

Hoskins and Himmelblau (1988) explore the characteristics of ANNs desirable for knowledge representation in processes and illustrate their discussion with an account of the use of an ANN to discriminate between faults in a simple process.

A further exploration of ANNs is described by Ungar, Powell and Kamens (1990). ANNs are able to learn non-linear and logical relationships as well as linear ones. They describe work using an ANN on a simple process in which a comparison is made between performance with discrete inputs, i.e. alarms, and with continuous inputs, i.e. sensor readings, and also work on the effect of noise.

Venkatasubramanian, Vaidyanathan and Yamamoto (1990) have studied the performance of ANNs under certain taxing conditions, including multiple faults and sensor faults.

M.A. Kramer and Leonard (1990) consider particularly the problems of extrapolation outside the conditions covered in the learning set. Such extrapolation becomes necessary when the learning set is undersized, when the parent distributions of fault classes undergo shifts, and when input data are corrupted by missing or biased sensors. They identify as a problem the inability of an ANN to detect when it lacks the data to effect a reliable classification.

30.45.10 Response advice systems

An account of a system for providing the operator with advice on the response to failures of critical safety functions is given by Nelson and co-workers (W.R. Nelson, 1984; W.R. Nelson and Blackman, 1985; W.R. Nelson and Jenkins 1985), who describe the Response Tree Evaluation project, one of those initiated following Three Mile Island. The purpose of the system is to select a response to provide by alternative means the safety function which has been disabled. The program creates a goal tree for the provision of the function, evaluates the availability of the various units, and searches for success paths. The search can be quite complex, since in general there is redundancy not only between units but within them.

Reference has already been made to the work of Chen and Modarres (1992) on the expert system FAX for the diagnosis of faults and advice on corrective actions.

30.45.11 Influence modelling and assessment system

The bulk of the work described so far deals with engineering problems of alarm diagnosis. It is necessary, however, to consider the ultimate function of such a system. This function is to provide support to the process operator, unless he be completely eliminated. As discussed in Chapter 14, the provision of an effective computer-based aid for the handling of alarms is fraught with difficulty.

This problem has been addressed by Embrey (1986). He takes as his starting point the fact that whereas for most types of human error the probability of recovery tends to be high, for diagnosis it is low.

In order to aid diagnosis, it is necessary to have some appreciation of the way in which the operator goes about it. In one view, the operator uses two distinct approaches. The first is the use of relationships between symptoms and faults. These are the symptomatic rules, or S-rules. They may be formally represented as a fault-symptom matrix (FSM). The other approach is topographic search. In this mode the operator makes a series of good/bad assessments based on his knowledge of the locations of and relationships between system components. These are the topographic rules, or T-rules. Since the use of S-rules involves less effort, the operator will generally apply these first, before resorting to the T-rules.

The fault–symptom matrix has been quite widely used in the process industries, and can be a useful aid to symptom based diagnosis, but it is rather inflexible and does not accommodate changes over time. Alternatively, use may be made of symptom-based procedures. These effectively bypass overt diagnosis and proceed straight to actions. Such procedures have been developed for nuclear plants following the Three Mile Island incident, but seem less applicable to process plants which are much more varied.

The approach proposed by Embrey is the use of an influence modelling and assessment system (IMAS). The purpose of this is to assist an operator in making his own diagnosis, and more specifically to support the use of the T-rule approach. His understanding of the relationships in the process, both causes and consequences of events, is elicited and encoded as a subjective cause–consequence model (SCCM).

Whatever the merits of this particular system, it is well to give the human aspect of fault administration its due share of attention.

30.46 Malfunction Detection

The third aspect of process monitoring is malfunction detection. The process computer can be used to detect or assist the operator to detect malfunctions before these give rise to alarm conditions. Malfunction detection, particularly in instruments, by the process operator, has been discussed in Chapter 14. Here consideration is given to the exploitation of the computer's potential in this area.

There are two basic methods of detecting malfunction in an equipment. These are to monitor (1) equipment performance and (2) equipment condition. The checking of performance is exemplified by the determination of the characteristic of a pump or of the heat transfer coefficient of a heat exchanger, while the checking of a condition is illustrated by the measurement of a compressor bearing temperature or the observation of leakage on a valve.

A classification of general methods of detecting malfunction in plant equipment such as compressors or heat exchangers, is as follows:

(1) process variable incorrect;
(2) equipment parameter incorrect;
(3) equipment relationship incorrect;
(4) equipment status incorrect;
(5) equipment condition faulty.

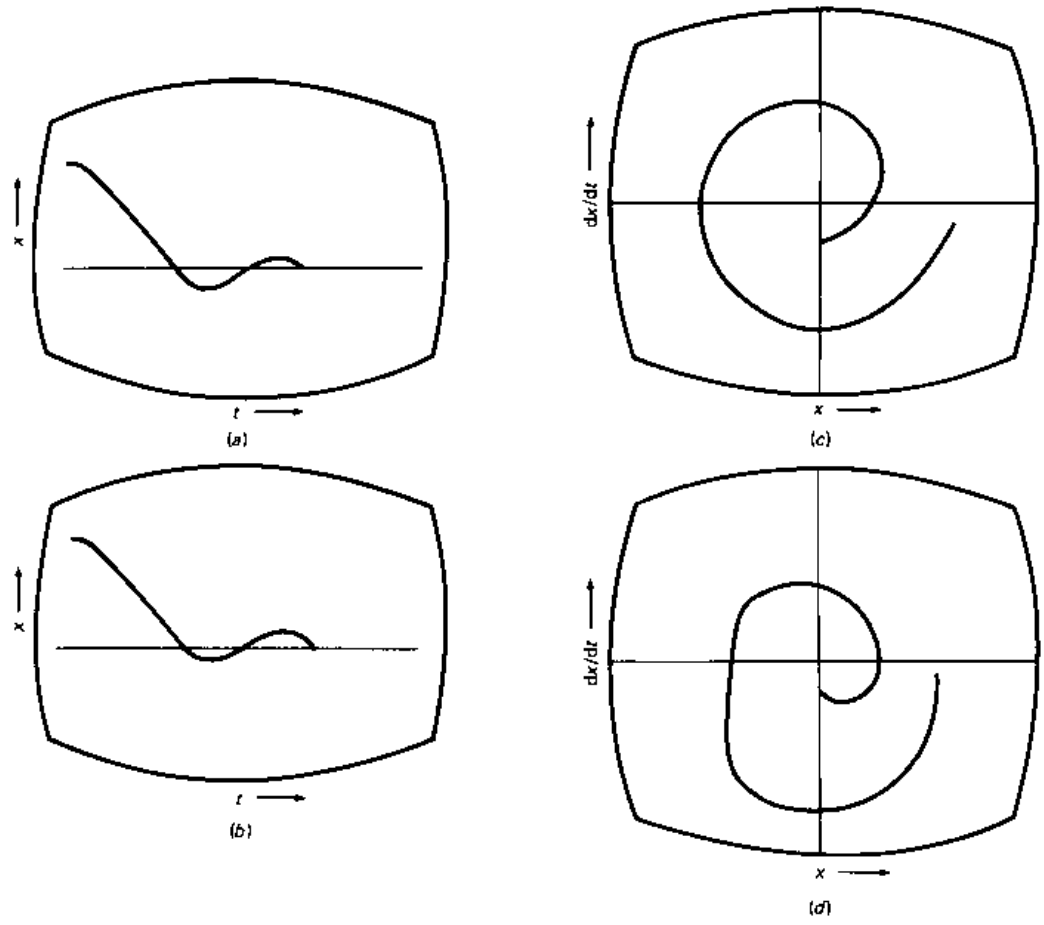


Figure 30.38 *Computer graphic displays for malfunction detection: phase plane plot of engine gimbal (after H.H. Bowen, 1967): (a) step response plot – device healthy; (b) step response plot – device unhealthy; (c) phase plane plot – device healthy; (d) phase plane plot – device unhealthy (Courtesy of Taylor & Francis Ltd)*

Probably the most common method of detection is from the fact that one or more process variables show the wrong value. Another check is that on a single parameter of the equipment, such as the efficiency of a compressor. Or a check may be made on a simple relationship such as the characteristics of a pump. Certain types of equipment, particularly mechanical handling equipment and regulating elements, have discrete states which they should be in at various stages of process operation, and a check may therefore be made on equipment status. Alternatively, the equipment condition may be checked with respect to features such as vibration. The classification of checks for malfunction detection in instruments has been given in Table 14.6.

The condition monitoring of plant equipment is an important activity on process plants and involves the use of specialized instrumentation and the interpretation of the signals obtained, and is described in Chapter 19. The aspect of interest here is the role of the computer as an aid in this area.

The types of function which the computer can perform include scanning, smoothing and comparing signals, calculating indirect measurements, processing information through simple correlations and models, and generating displays.

The use of process computers for malfunction detection as opposed to alarm monitoring was rather slow to develop. For some time the widespread activity of condition monitoring made relatively little use of process computers. There has been, however, a gradual increase in the role of the computer in support of this function.

The use of a computer to monitor reciprocating compressor performance by calculating quantities such as gas leakage and efficiency has been reported by

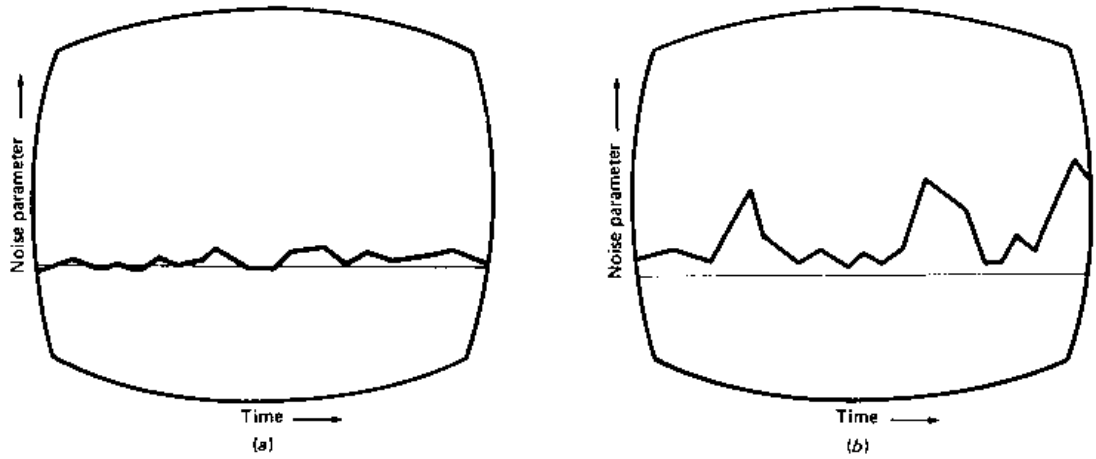


Figure 30.39 *Computer graphic displays for malfunction detection: noise parameter plot for a failing thermocouple (after Anyakora and Lees, 1973): (a) thermocouple healthy; (b) thermocouple failing. The horizontal line represents the mean value of the noise parameter for a healthy instrument*

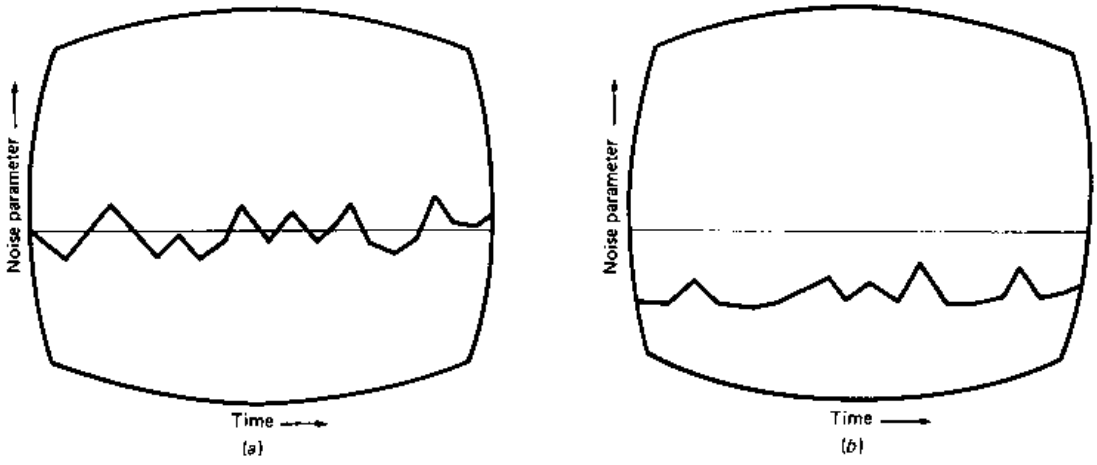


Figure 30.40 *Computer graphic displays for malfunction detection: noise parameter plot for a frozen flowmeter (after Anyakora and Lees, 1973). (a) Flowmeter healthy; (b) flowmeter with impulse lines frozen. The horizontal line represents the mean value of the noise parameter for a healthy instrument*

Gallier (1968). Several different schemes are described with different instrumentation requirements. Benefits adduced by the author are the early detection of malfunction and also improvement of the load between parallel compressors.

In another installation where reciprocating compressors are used in the on–off mode to maintain the pressure of air in receivers within fixed limits, the amount of time during which the compressors are on is used as a simple indication of possible trouble.

Models of large centrifugal compressors are sometimes used for optimization purposes, but such models may also be used to monitor compressor characteristics as a means of malfunction detection. Other applications of the use of process computers in detecting malfunction in process machinery have been described in Chapter 19.

Monitoring need not necessarily be confined to process machinery. The calculation of heat transfer coefficients in plant equipment by the process computer is quite widely practised.

The principal method currently used for early detection of malfunction, however, is the measurement and analysis of equipment characteristics such as vibration, using special instruments. The signals obtained are often rather noisy and individual to the equipment. These characteristics suggest that there is scope for the use of

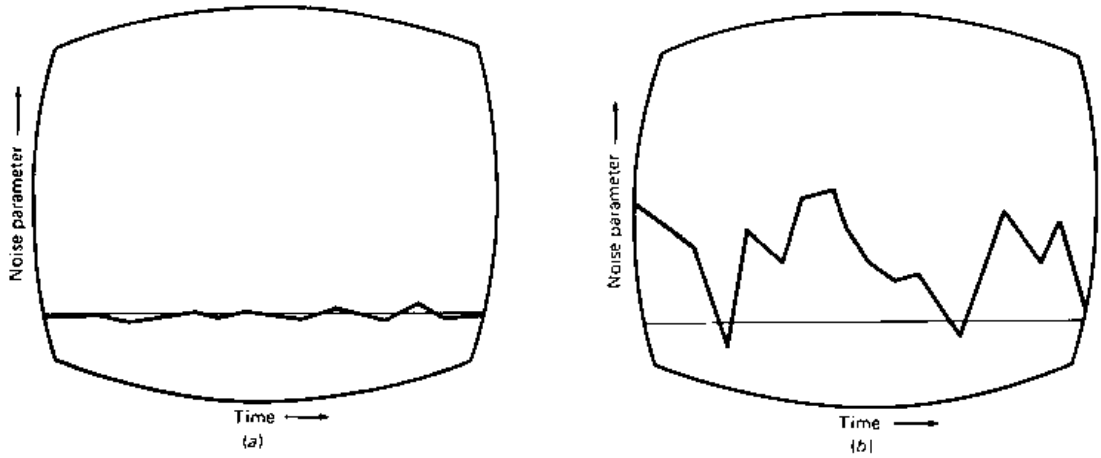


Figure 30.41 *Computer graphic displays for malfunction detection: noise parameter plot for a sticking control valve (after Anyakora and Lees, 1973): (a) valve healthy; (b) valve sticking. The horizontal line represents the mean value of the noise parameter for a healthy instrument*

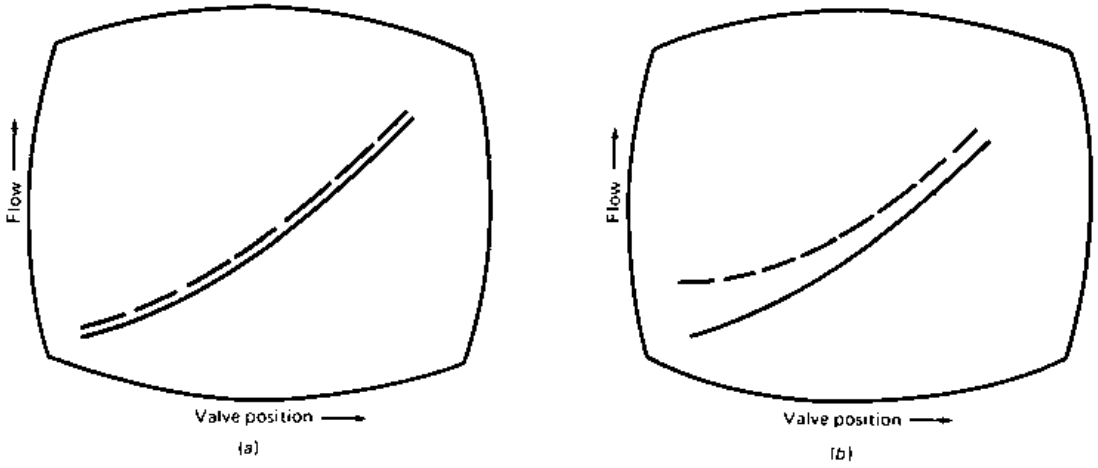


Figure 30.42 *Computer graphic displays for malfunction detection: measured and inferred flow in a flow control loop (after Bellingham and Lees, 1977b): (a) loop healthy; (b) loop with flowmeter zero error. (— — — —) measured flow; (———) flow calculated from the valve position*

the computer's ability for the smoothing and display of information.

Another related development is the monitoring of undesirable operating conditions on the plant. This can be due to maloperation by the operator and it is sometimes possible for the computer to monitor this and display it to the operator. The display to the operator of the rate at which he is using up the creep life of furnace tubes is one industrial example of this.

The same principle has been applied in the monitoring of control of ships, where the degree of maloperation is measured by instrumentation and analysed using estimation theory. The data are then displayed to the operator as a signal (Asbjornsen, 1976).

Of particular importance to the computer system itself is the correct operation of the sensors and valves which are connected to it. The detection of malfunction in these instruments is now considered.

30.46.1 Malfunction detection in individual instruments

The detection of incipient malfunction in instruments may follow one of two approaches. In the first the check is made on an individual instrument, or at least a limited set such as a control loop, whilst in the second it is

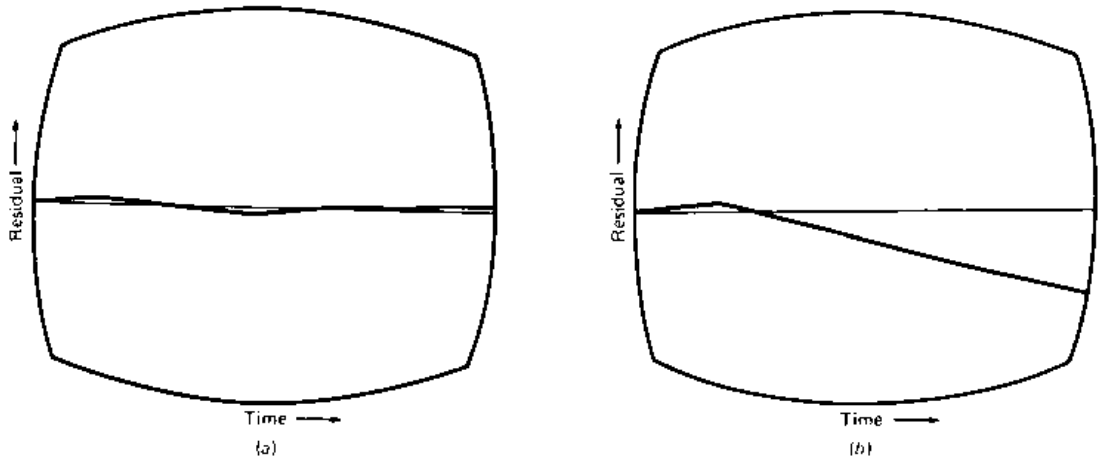


Figure 30.43 *Computer graphic displays for malfunction detection: error residual in a flow control loop (after Bellingham and Lees, 1977b): (a) loop healthy; (b) loop with flowmeter zero error. The horizontal line represents the mean value of the residual for a healthy loop*

made on an ensemble of instruments, often in different parts of the plant.

Some of the checks made by the process operator on individual instruments and control loops have already been described in Chapter 14. Many of the developments in checks which may be made by the process computer have analogues in those made by the operator. In those systems where computer checks on instruments have been implemented, the favoured methods generally have been checks on 'hardover' zero or full-scale signals and on an excessive rate of change in signals.

These checks, however, by no means exhaust the potential. The noise on a signal is often a useful indication of malfunction. Anyakora and Lees (1973) have described a method in which the noisiness of the signal is used as a check. The smoothed signal is subtracted from the crude signal to yield a noise residue, and a noise parameter is calculated from the sum of the squares of the noise residue taken over a group of readings. The technique has been used to detect the onset of malfunction in a thermocouple and in a flowmeter with freezing impulse lines. A modification of the technique has also been used to detect incipient stickiness in control valves. In this case the noise residue was the difference between the desired and actual valve positions, the latter being measured by a potentiometer.

A method of detecting malfunction in any of the elements in a flow control loop based on a comparison of the measured flow with the control valve position has been developed by Bellingham and Lees (1977b). The principle is that the valve position gives an additional indication of flow with which the actual flow measurement can be compared. The method assumes that the relation between flow and pressure drop through the system remains constant. In the simplest case where the valve can be stroked over its whole range, the relation between the valve position and flow, or the valve characteristic, can be obtained, and any departures from the original characteristic can be determined. It was found in practice that it is preferable to detect such divergence using a simple tracking estimator which generates an error residual. This method does not require the full stroking of the valve. The detection of faults ranging from flowmeter zero error to valve trim damage was demonstrated.

This approach has also been applied by Bellingham and Lees (1977a) to the general control loop such as level, pressure and temperature, in which the measurements and the valve position are not as directly linked as in the flow control loop. The loop studied was a level control loop. In this work use was made of an estimation method based on Kalman filtering. Again the method was successful in detecting faults ranging from level meter zero error to valve trim damage. A rather cruder check based on the same principle on the feed flow to a cement kiln has been described by Barton *et al.* (1970).

Most of these techniques may be used either to carry out an automatic check or to provide a display to assist the operator in checking. A display specifically developed to allow visual checking by the operator is that of an engine gimbal developed by H.H. Bowen (1967) and illustrated in Figure 30.38. Figures 30.38(a) and 30.38(b) show the step response of healthy and unhealthy gimbals, respectively; it is difficult to distinguish between them. Figures 30.38(c) and 30.38(d) show the corresponding phase plane displays; the difference is quite clear.

Figures 30.39–30.41 illustrate the type of display which may be generated using the Anyakora and Lees (1973) technique of monitoring the instrument noise. Figures 30.39(a) and 30.40(b) show, the noise parameter plots for a healthy and for a failing thermocouple, Figures 30.40(a) and 30.40(b) show those for a healthy flowmeter and for one with frozen impulse lines, and Figure 30.41(a) and 30.41(b) show those for a healthy and for a sticking control valve.

The display shown in Figure 30.42 is a plot given by Bellingham and Lees (1977b) of the flow in a flow control loop as measured by the flowmeter (dotted line)

and as inferred from the control valve position (full line). The generation of this display requires the valve to be stroked over the whole range. Figures 30.42(a) and 30.42(b) show healthy and unhealthy loops, respectively. Another display is based on the generation of a residual error, which is more suitable if valve travel is limited. Figures 30.43(a) and 30.43(b) illustrate the display of this residual for the healthy and unhealthy cases.

This account is perhaps enough to give a flavour of the work on malfunction detection. It illustrates the allocation to the computer and the operator of functions which they perform well, such as signal processing and display generation on the one hand and pattern recognition on the other.

More detailed accounts of malfunction detection have been given by Anyakora and Lees (1972a,b), E. Edwards and Lees (1973) and Whitman (1972).

30.46.2 Malfunction detection in instrument ensembles

The alternative approach to instrument malfunction detection is to check whole ensembles of instruments. As stated in Section 30.44, it is not uncommon to check the consistency of sets of instrument readings which determine a relationship such as a mass or energy balance, although generally the concern here is more with data reconciliation than malfunction detection.

The checking of ensembles of instrument readings for internal consistency has received increasing attention. Reviews of work in this area have been given by Willsky (1976), Himmelblau (1978) and Venkateswarlu, Gangiah and Rao (1992). An early example of work in this area is that of Goldmann and Sargent (1971), who used Kalman filtering to track the unsteady-state behaviour of the system and to detect sensor drift.

Venkateswarlu, Gangiah and Rao classify the quantitative processing of sensor data into three broad categories: data reconciliation and rectification; state estimation; and filtering and parameter identification. Work on data reconciliation is illustrated by that of Mah, Stanley and Downing (1976), Stanley and Mah (1977), Romagnoli and Stephanopoulos (1981), Madron (1985), and Narasimhan and Mah (1987). Work on state estimation methods is illustrated by that of Willsky (1976), Watanabe and Himmelblau (1983) and Frank (1987); and work on filtering and parameter estimation is illustrated by that of Isermann (1984), Park and Himmelblau (1983), Watanabe and Himmelblau (1983, 1984) and Dalle Molle and Himmelblau (1987).

30.47 Notation

Section 30.8

C	certainty
CF	certainty factor

Section 30.9

f	Bayesian factor
LN	logical necessity
LS	logical sufficiency
O	odds
P	probability
w	weight of evidence

Section 30.10

F	attribute
n	number of items in set
n_{F}	number of items with attribute F
Q	fuzzy quantifier
$\mu_{\mathrm{A}}(x)$	grade of membership of x in A
$\mu_{\mathrm{F}}(x)$	membership function for attribute F
$\mu_{\mathrm{Q}}(x)$	membership function
τ	truth value

Section 30.20

G_j	information gain for attribute j
H_{c}	expected information content of message
H_j	information content for attribute j at node
H_{jk}	information content for attribute j in branch k at node
j	attribute counter
k	branch counter
p_{jk}	proportion of objects having attribute j in branch k at node

Section 30.26

L	level
Q	flow
t	time

Subscripts:

1	inlet
2	outlet

Section 30.36

L	level
G	pressure differential
P	pressure
Q	flow
U	temperature in reverse flow

Subscripts:

1	inlet
2	outlet

Section 30.42

As Section 30.36